LUBRICANT BASE OIL AND WAX PROCESSING

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Preface

The purpose of this book is to provide information and references on the processes being used for lubricant base oil and wax manufacture. This book will be of interest to base oil and wax refiners, formulators, marketers, and consumers because it provides the information on lubricant base oil processing most often missing in reference books on petroleum processing that deal primarily with manufacturing fuels and/or petrochemicals. This book also supplements the reference books concerned with tribology and the formulation of lubricants.

The information contained here is based on many years of experience with base oil and wax processing and many discussions with or publications by various petroleum refiners and licensors of base oil and wax refining processes. Although the patent literature offers much useful information on current or proposed processes, it has been extensively reviewed but is not referenced in this text because the use of many of the patented processes is not known. Some of this technology is not being used, is proprietary, or is restricted by secrecy and licensing agreements between the licensors and users of the technology.

The preparation of this reference text was driven in part by the fact that the last reference text dealing exclusively with base oil and wax processing was *Modern Methods of Refining Lubricating Oils* by V. A. Kalichevsky, published in 1938. Since its publication, improvements have been made to these processes and new processes have been developed. The processes cur-

rently being used are described in periodicals and in papers presented at associations of the petroleum refiners and technical society meetings, with general descriptions or overviews of these processes provided in texts dealing with petroleum refining or lubrication. In many cases, an occasional chapter dealing with only one process or a process offered by a single licensor is presented. In order to obtain useful information one often must network with other refiners, consult with engineering contractors or enter into secrecy agreements or licenses with licensors of the technology.

It would be impossible to list all the people who have contributed to this book or helped put it together. It is a compilation of information developed by the author, coworkers, and employees of other petroleum refiners. It also includes contributions from employees of governmental laboratories, engineering and construction firms, and educational institutions. Although it is impossible to acknowledge everyone, the following individuals and groups must be singled out for a special thank you: Texaco, Inc., for permission to publish and assistance in preparation of this book; Dr. R. M. Gipson for his encouragement and allowing me the time which permitted preparation of the text; Messrs. G. F. Prescott, C. H. Schrader, and other researchers at Texaco for their review, comments, and constructive criticism; Messrs. Don Thomas and L. J. Hodgkinson for preparing the graphics. A special thanks goes to my wife, June, for many years of support and encouragement which permitted me the time needed to accumulate and edit the information reported in the book.

Avilino Sequeira, Jr.

Contents

Preface *iii*

1. Lubricant Base Oil and Wax Processing Overview 1
   - I. Introduction 1
   - II. Manufacturing Processes 2
   - III. Effects of Lubricant Base Oil Processes 5
   - IV. Formulated Products 5
   - V. Additives 6
   - VI. Lubricant Base Oil and Wax Processing Profile 6
   - VII. Supply and Demand of Lubricant Base Oils 13
   - References 15
   - Additional Readings 15

2. Crude Oils, Base Oils, and Petroleum Wax 17
   - I. Crude Oils: Composition 17
   - II. Classification of Crude Oils 23
   - III. Crude Oil Properties 23
   - IV. Refinery Products 24
   - V. Crude Evaluation Methods 24
   - VI. Base Oil Types and Properties 28
   - VII. Formulated Lubricants 35
   - VIII. Speciality Oils 35
   - IX. Waxes 37
   - References 40
   - Additional Readings 41

3. Lubricant Base Oil Distillation 42

I. Introduction 42
II. Crude Desalting 42
III. Distillation 43
IV. Investment and Utility Requirements 50
References 51
Additional Readings 51

4. Lubricant Base Oil Deasphalting Processes 53

I. Introduction 53
II. Deasphalting Process Variables 55
III. Process Flow 61
IV. Solvent Recovery Techniques 70
V. Deasphalting Devices 72
VI. Investment and Utility Requirements 75
References 78
Additional Readings 79

5. Solvent Refining of Lubricant Base Oil Stocks 81

I. Introduction 81
II. Processes 82
III. Process Variables and Operating Conditions 95
IV. Extraction Devices 105
V. Conversion of Furfural and Phenol Units to MP 110
VI. Energy Reduction Techniques 113
VII. Investment and Utility Requirements 116
References 117
Additional Readings 118

6. Lubricant Base Oil Hydrogen Refining Processes 119

I. Introduction 119
II. Hydrocracking Processes 121
III. Hydrorefining Processes 138
References 148
Additional Readings 150

7. Solvent Dewaxing and Wax Deoiling Processes 153

I. Introduction 153
II. Solvent Dewaxing and Wax Deoiling Processes 155
III. Wax Fractionation (Deoiling) Processes 162
IV. Process Variables 165

V. Solvent Recovery 186
VI. Other Energy Reduction Techniques 189
VII. Investment and Utility Requirements 190
References 190
Additional Readings 192

8. Catalytic Dewaxing Processes 194

I. Introduction 194
II. Processes 196
III. Catalytic Dewaxing Fundamentals 204
IV. Investment Costs and Utilities Requirements 221
References 222
Additional Readings 224

9. Lubricant Base Oil Finishing Processes 225

I. Introduction 225
II. Sulfuric Acid Treating Processes 226
III. Clay Treating Processes 229
IV. Hydrogen Finishing Processes 232
V. Wax Finishing 240
VI. Solvent Refining 244
References 244
Additional Readings 245

10. Used Oil Recycling Processes 247

I. Introduction 247
II. Reclaiming Techniques 247
III. Major Re-Refining Processes 248
IV. Other Reclaiming Processes 251
V. Economics of Used Oil Reclaiming 252
References 255
Additional Readings 256

Appendix *259*

I. Nomenclature 259
II. Glossary of Acronyms and Terms 262
III. Updating Refinery Construction Costs 278
IV. Nelson–Farrar Refinery Construction Indexes 279
V. Conversion Factors 281

Index *283*

LUBRICANT BASE OIL AND WAX PROCESSING

1

Lubricant Base Oil and Wax Processing Overview

I. INTRODUCTION

In the early days of the petroleum industry, only those crude fractions of appropriate gravity and viscosity (from Pennsylvania crudes) were considered suitable for the manufacture of lubricant base oils used in automobile engines and other machines operated at high speed. Pennsylvania feedstocks required only acid treating and cold wax settling to manufacture suitable lubricant base stocks of high viscosity index. The lubricant base oil fractions from other crudes contain more aromatics and are of lower viscosity index which detract from their use as base oils. As the demand for base oils increased petroleum refiners developed many chemical and solvent treating processes which would upgrade the less desirable crude fractions into suitable base oils. Hydrogenation processes have been developed which are used to upgrade the fractions from the less desirable crude oils and fractions from crude oils which cannot be upgraded to the desired quality levels by the solvent extraction processes. Conventional lubricant base oil processing, therefore, has a different meaning to different refiners and to personnel at different base oil plants for the same refiner because of the different types of crude oils used and variety of lubricant base stocks which are manufactured using a variety of processes and process combinations.

II. MANUFACTURING PROCESSES [1]

The manufacture of lubricant base oils consists of five basic steps: 1) distillation and 2) deasphalting to prepare the feedstocks, 3) solvent or hydrogen refining to improve viscosity index and remove undesirable constituents, 4) solvent or catalytic dewaxing to remove wax and improve the low temperature properties of paraffinic base oils and 5) clay or hydrogen finishing to improve the color, stability and quality of the lubricant base stocks. Figures 1.1 and 1.2 illustrate some of the process combinations used to manufacture paraffinic and naphthenic base oils and by-products, respectively [1].

The lubricant base oil and wax refiner usually selects the mix or combination of processes that best matches the products of manufacture from the crude sources available. The mix of processes used will also depend on the product slate at each location. In addition, restraints are placed on refiners in certain locations. These restraints are usually governmental policies that limit or prohibit the use of materials and/or technology which are developed outside their country.

A. Distillation

In a lubricant base oil and wax manufacturing plant, crude oil is first distilled in an atmospheric distillation unit (ADU) to remove gases, gasoline, naphthas, kerosine and light gas oil. The atmospheric residuum (reduced crude) is then

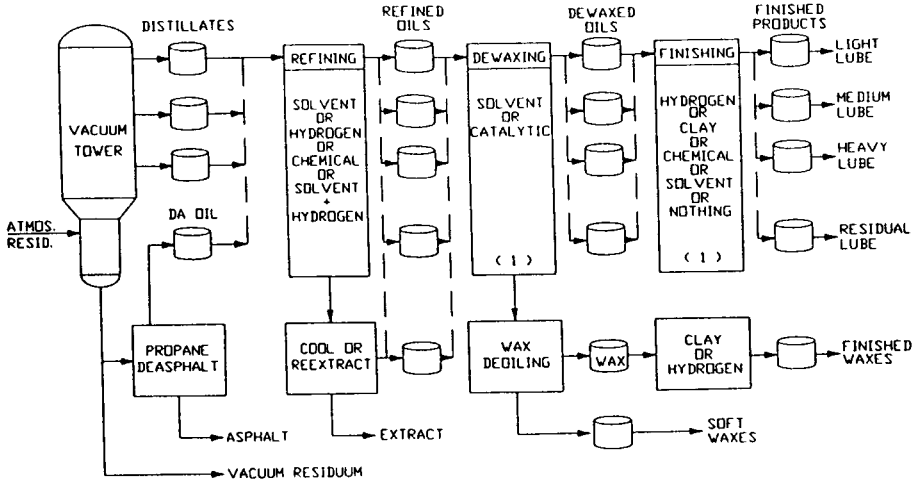

Figure 1.1 Process flow for manufacture of paraffinic base oils. Dewaxing and finishing processes are frequently reversed. (Reprinted from Ref. [1].)

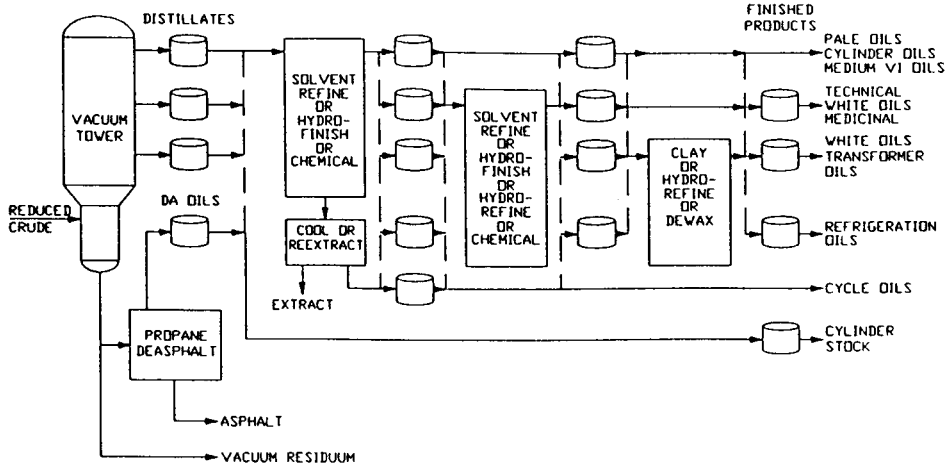

Figure 1.2 Process flow for manufacture of naphthenic base oils. (Reprinted from Ref. [1].)

fractionated in a vacuum distillation unit (VDU) into fractions of the desired viscosity and flash for further processing.

B. Deasphalting

The vacuum residuum contains recoverable lubricant stock of high viscosity mixed with asphalt and resins. This oil is separated from the asphalt and resins using propane deasphalting, an extractive precipitation process.

C. Refining

The deasphalted oil and the distillates usually contain undesirable constituents such as aromatics and naphthenes and these must be removed to yield an oil of high viscosity index and high lubricating quality. These undesirable constituents are removed by treating the stocks separately with a solvent (furfural, phenol, N-methyl-2-pyrrolidone or liquid sulfur dioxide) which selectively removes (extracts) these constituents from the oil. The extract, containing the undesirable materials which have been removed, may be used as FCCU (catalytic cracking) or coker feedstock, blended into fuel oil, hydrocracked or used as a rubber extender oil.

Hydroextraction, a mild solvent extraction of distillates and deasphalted oils followed by moderate severity hydrotreating (mild hydrocracking) is conducted by some refiners for the purpose of decreasing hydrogen consumption and increasing refined oil yields.

Hydrocracking followed by distillation is sometimes used as an alternative to solvent refining. These processes are the severe hydrogenation processes which convert (hydrocrack and isomerize) low VI materials into base stock or fuel fractions.

The stabilization of hydrocracked base oils is usually done using a high pressure–low temperature hydrogenation called high severity hydrofinishing, speciality products hydrogenation or hydrorefining. Solvent extraction is also used to stabilize hydrocracked base oils.

Hystarting or the removal of sulfur, nitrogen and oxygen by hydrogenation prior to solvent extraction is used for some feedstocks by some refiners. When conducted at sufficiently high temperature and pressure this process will also saturate some of the aromatics.

D. Dewaxing

The refined paraffinic oils contain waxes which crystallize out at low temperatures, thus reducing the fluidity of these oils which have a high pour point. In order to produce a lubricating oil which is not a solid at low temperatures, the wax is removed by solvent dewaxing (a crystallization–filtration process). The slack waxes from the dewaxing process are used as FCCU feed or deoiled using a warm-up or recrystallization process to produce a hard wax and a soft wax. The soft wax or foots oil is frequently used as a seal oil or as FCCU feedstock.

A selective hydrocracking process called catalytic dewaxing is used as an alternative to solvent dewaxing and hydrogen finishing for the removal of wax and finishing of lubricant base oils. No wax is produced from catalytic dewaxing unless the desired wax is removed by solvent dewaxing prior to catalytic dewaxing.

E. Finishing

Both the dewaxed oil and the product wax are normally hydrofinished or treated with adsorbent clay to meet the color and oxidation stability requirements of a marketable product. A severe hydrogen finishing process, hydrorefining, is used to remove large amounts of sulfur and nitrogen and trace impurities in the manufacture of food grade wax and pharmaceutical grade white oils or to stabilize base oils produced by hydrocracking. Solvent refining is also used to stabilize hydrocracked base oils.

F. Product Formulation

The finished base oils are then blended with one another and with additives to produce the desired high grade lubricants. Speciality oils such as refrigeration oils and white oils are manufactured using the conventional processes in conjunction with acid and clay treating or hydrorefining processes.

III. EFFECTS OF LUBRICANT BASE OIL PROCESSES [2]

The usual effects of base oil processes on the chemical composition and physical properties of base oil feedstocks are summarized in Table 1.1. Although the base oil processes were developed for a specific purpose, they result in several different changes in chemical composition and physical properties. For example, solvent refining was developed to improve the viscosity index and quality of base stocks by removing aromatics. A reduction in sulfur and nitrogen content, an increase in API gravity, a decrease in viscosity and an improvement in color are also obtained. In recent years there has been an increase in the use of solvent extraction and hydrorefining to reduce the toxicological aggressiveness of naphthene pale oils.

IV. FORMULATED PRODUCTS [3]

In order to properly lubricate, a lubricant must reduce friction and wear and prevent scuffing and seizure of moving parts. These basic lubricating functions are accomplished by creating an oil film between the moving parts. Depending on the lubricating oil viscosity, the dynamics of the mechanism being lubri-

Table 1.1 Usual Effect of Manufacturing Processes on the Chemical Composition and Properties of Base Oils

Constituent	Deasphalting	Refining	Dewaxing	Finishing
Asphaltenes	Decrease	Decrease	Increase	Decrease
Resins	Decrease	Decrease	Increase	Decrease
Aromatics	Decrease	Decrease	Increase	Depends
Naphthenes	Increase	Increase	Increase	Depends
Paraffins	Increase	Increase	Decrease	Depends
Wax content	Increase	Increase	Decrease	Nil
Nitrogen	Decrease	Decrease	Increase	Decrease
Sulfur	Decrease	Decrease	Increase	Decrease
Property				
Specific gravity	Decrease	Decrease	Increase	Decrease
Flash point	Nil	Nil	Nil	Nil
Viscosity	Decrease	Decrease	Increase	Nil
Viscosity index	Increase	Increase	Decrease	Nil
Pour point	Increase	Increase	Decrease	Increase
Color	Improve	Improve	Depends	Improve
Stability	Improve	Improve	Nil	Improve
Additive response	Improve	Improve	Nil	Improve

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cated and its cycle, there are also times when minute to substantial areas of metal to metal contact will exist. The lubricating oil must be capable of modifying surfaces such that friction and wear are kept to a minimum during these times.

Lubricating oils must also perform a large number of other functions. Some are related to the specific equipment being lubricated and some are common to all equipment. These functions include removal of heat, prevention of rust and corrosion, prevention of excessive deposits, dispersion of use-generated contaminants, maintenance of water separability and emulsibility, maintenance of sealing in critical parts, and maintenance of resistance to degradation in the presence of oxygen and catalytic materials. All of these functions must be performed while providing an acceptable drain interval. These basic lubricating functions are provided by the base oil component while many of the remaining functions are either provided or enhanced by the use of additives.

V. ADDITIVES

The naphthenic, paraffinic, or synthetic base oils or blends of these base oils and/or additives are used to make formulated lubricants. Tables 1.2 and 1.3 provide a listing of the types of additives used to formulate automotive and industrial lubricants. Additional information concerning the purpose, function and typical compounds used as additives may be found in most reference books dealing with tribology or other publications such as *Lubrication* [3].

VI. LUBRICANT BASE OIL AND WAX PROCESSING PROFILE

Capacities of base oil and wax refiners are difficult to obtain because most refiners do not publish this information. In addition some refiners overstate

Table 1.2 Additives for Automotive Lubricants

Surface protective additives	Performance additive	Lubricant protective additives
Antiwear agents	Pour point depressants	Antifoamants
Corrosion inhibitors	Seal swell agents	Antioxidants
Detergents	Viscosity index (VI) improvers	Metal deactivators
Dispersants		
Extreme pressure (EP)		
Friction modifiers		
Rust inhibitors		

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Table 1.3 Additives for Industrial Lubricants

Surface protective additives	Performance additives	Lubricant protective additives	Miscellaneous additives
Oiliness agents	Pour point depressants	Antioxidants	Dyes
Extreme pressure agents	Vis. index improvers	Antifoamants	Odorants
Antiwear agents	Emulsifiers	Bactericides	
Corrosion inhibitors	Demulsifiers	Bacteriostats	
Rust inhibitors	Tackiness agents	Fungicides	

Reprinted from Ref. [3] by courtesy of Texaco, Inc.

capacity while others understate capacity and the effect of crude source on capacity is not disclosed. As a result recently published information [4,5,6,7,8,9] has been used to prepare an estimate of the worldwide lubricants base oil processing capacity. These data summarized in Table 1.5 have been adjusted for known additions and shutdowns. The data summarized in Table 1.4 indicate that total base oil manufacturing capacity ranges from about 725,000 to about 950,000 barrels per calendar day. The reasons for these differences in reported capacity are not known. It is believed that the higher manufacturing capacities are closer to the actual base oil capacity and that capacities could be increased significantly by selection of higher quality crude oils by some of the base oil refiners.

The capacities of the United States base oil plants and wax plants are summarized in Tables 1.5 and 1.6, respectively [9]. The base oil and wax capacities as a percent of crude capacity are shown in Table 1.6. These data show that base oil capacity ranges from about 1 to 69 percent of crude capacity and averages 5.2 percent of crude capacity for all base oil manufacturers. CitCon's crude capacity is not included because they receive reduced crude from one of their owners. Total wax manufacture averages about 0.7 percent of crude capacity for all base oil and wax manufacturers. Base oil manufacture averages 1.3 percent of the 15 million barrels per operating day of crude capacity and wax manufacture averages less than 0.2 percent of crude capacity in the United States. Similar data extracted from the 1993 NPRA survey for base oil and wax manufacture in Canada are summarized in Table 1.7.

The trends in U.S. base oil and wax manufacturing capacity from January 1, 1976 through January 1, 1993 are summarized in Table 1.8. These data taken from the NPRA Annual Surveys show that base oil capacity increased from about 228,000 BPCD in 1976 to about 236,000 BPCD in 1984 and decreased to about 203,000 BPCD in 1993; a 13.6 percent decrease from the high nameplate capacity of 1984.

Table 1.4 Estimated Worldwide Lubricant Base Oil Nameplate Capacity

Country	1993 Nameplate capacity, BPCD	
	Vacuum distillation	Base oils
Algeria	14,500	2,300–2,400
Argentina	303,432	4,700–5,763
Australia	158,800	12,900–21,360
Austria	69,600	1,400
Bolivia	2,210	800
Brazil	725,935	14,500–23,605
Bulgaria	NA	3,100–4,200
Canada	671,950	16,500–18,760
Canary Islands		1,000
Columbia	138,000	2,600–3,300
C.I.S. (Former USSR)	2,446,640	168,500–228,660
Czechoslovakia	59,962	4,700–5,800
Egypt	47,000	3,900–4,900
France	759,150	33,200–36,100
Germany	1,016,700	17,800–27,800
Greece	65,600	3,000–3,500
Hungary	113,500	4,000–4,200
India	368,400	12,100–13,350
Indonesia	238,400	4,900–5,000
Iran	284,640	5,200–10,920
Iraq	82,650	4,100–10,168
Israel	84,000	1,400–2,500
Italy	837,668	23,100–32,800
Japan	1,659,965	42,900–50,895
Korea, South	95,400	5,200–8,500
Libya	1,000	600
Mexico	712,700	10,000–19,000
Morocco	27,400	1,900–2,100
Myanmar	4000	500
Netherlands	425,600	11,400–11,500
Netherlands Antilles	315,000	8,600–12,000
Nigeria	124,490	3,878–4,800
Pakistan	12,350	3,563–4,300
Peru	45,150	700–1,200
Philippines	66,900	3,400
Poland	135,500	5,500–7,800
Portugal	53,200	2,900–3,000
Puerto Rico	67,000	8,800–9,200
Romania	321,934	2,900–11,700
Saudi Arabia	425,555	4,700–5,000
Singapore	273,650	12,000–15,800

(*continued*)

Table 1.4 Continued

Country	1993 Nameplate capacity, BPCD	
	Vacuum distillation	Base oils
South Africa	102,000	3,000–6,000
Spain	404,800	7,700–13,000
Sweden	135,000	2,500–3,300
Taiwan	111,700	3,960–4,700
Trinidad	130,000	2,700–2,800
Turkey	156,438	4,000–5,385
United Kingdom	804,850	21,600–28,300
United States	6,634,353	193,776–200,900
Venezuela	548,370	6,700–8,718
Yugoslavia	163,059	4,900
TOTAL	23,186,265	724,277–951,265
Total Crude Capacity	73,186,265	
Total No. Refineries	712	

Prepared from Refs. [4,5,6,7,8,9].

The data show that paraffinic lube manufacturing capacity peaked at 176,900 BPCD in 1981 and decreased by about 15 percent to 150,300 BPCD by 1993; naphthenic lube capacity remained essentially constant through 1989 and decreased by about 12 percent between 1989 and 1993. Wax capacity has increased by about 12 percent between 1976 and 1993. Crude capacity of the lube and wax refineries decreased from 5,486,600 to 3,876,700 BPCD or about 25 percent during this period. Base oil capacity on the other hand has increased from about 4 to 5 percent of crude capacity.

The capacities of the seven leading U.S. base oil and wax refiners in 1993 are shown in Table 1.9 for the period 1979–1993. These data, taken from the NPRA surveys, show that the current seven leading base oil refiners have about 65 percent of the nameplate capacity. Although the leading five refiners during each of these years has changed, it is interesting to note that the leading five refiners, in any given year, accounted for about 55 percent of the nameplate capacity. The remaining 45 percent of total lube and wax capacity was distributed among the remaining refiners, 25 in 1979 and 16 in 1993. The data also show that the number of base oil and wax plants has declined by about 33 percent during this period. The base oil and wax capacity of the refiners listed has varied during the 1979–1993 period because of revamps, shutdowns, and accidents which resulted in temporary shut-downs of some process facilities.

Table 1.5 Capacities of United States Base Oil Manufacturing Plants—January 1, 1993

Refiner, location	Capacity, 1000 BPCD			Percent of crude
	Paraffin	Naphthene	Total	
Amoco, Whiting, IN	6.2	—	6.2	17.7
Ashland, Catlettsburg, KY	8.0	—	6.0	3.9
Calumet, Princeton, LA	—	5.5	5.5	68.8
Chevron, Richmond, CA	10.0	—	10.0	4.4
Cit-Con, Lake Charles, LA	8.9	—	8.9	NA
Cross Oil, Smackover, AK	—	4.0	4.0	57.1
Diamond Shamrock, Three Rivers, TX	—	1.4	1.4	1.9
Ergon, Vicksburg, MS	—	6.0	6.0	24.0
Exxon, Baton Rouge, LA	13.8	—	13.8	4.4
Exxon, Baytown, TX	18.0	13.2	31.2	7.9
Lyondell, Houston, TX	3.8	3.2	7.0	2.7
Mobil, Beaumont, TX	10.1	—	10.1	3.3
Mobil, Paulsboro, NJ	8.2	—	8.2	7.3
Pennzoil, Rouseville, PA	4.4	—	4.4	26.7
Pennzoil, Shreveport, LA	6.9	2.7	8.6	18.6
Petrowax PA, Smethport, PA	0.5	—	0.5	10.0
Quaker State, Newell, WVA	3.6	—	3.6	34.3
San Joaquin, Bakersfield, CA	—	2.9	2.9	13.8
Shell Oil, Deer Park, TX	4.5	5.0	9.5	4.4
Shell Oil, Martinez, CA	—	3.9	3.9	2.7
Shell Oil, Wood River, IL	5.0	—	5.0	1.8
Star Enterprise, Port Arthur, TX	18.5	—	18.5	7.4
Sun Company, Tulsa, OK	7.5	—	7.5	8.8
Sun Company, Yabucoa, Puerto Rico	8.8	—	8.8	10.3
Unocal Corporation, Rodeo, CA	4.6	—	4.6	6.3
Witco Chemical, Bradford, PA	2.1	—	2.1	21.0
Witco Chemical, Oildale, CA	—	5.3	5.3	48.1
Total	150.3	53.1	203.4	5.2

Prepared from the 1993 NPRA Survey, by permission of the NPRA.

A profile of the U.S. base oil refining process capacity as a percentage of crude capacity and base oil capacity is provided in Table 1.10. These data show a wide variation in each processing capacity and that base oil and wax processing capacity is about 20 percent of crude capacity and 388 percent of base oil capacity.

Table 1.6 Capacities of United States Wax Manufacturing Plants January 1, 1993

Refiner, location	Wax capacity, 1000 BPCD		
	Refined	Other	Total
Amoco, Whiting, IN	0.6	—	0.6
Ashland, Catlettsburg, KY	—	2.8	2.8
Chevron, Richmond, CA	1.2	1.0	2.2
Cit-Con, Lake Charles, LA	1.3	0.8	2.1
Exxon, Baton Rouge, LA	1.7	—	1.7
Exxon, Baytown, TX	—	1.8	1.8
Lyondell, Houston, TX	—	1.0	1.0
Mobil, Beaumont, TX	1.6	0.3	1.9
Pennzoil, Rouseville, PA	0.6	0.4	1.0
Pennzoil, Shreveport, LA	0.8	—	0.8
Petrolite, Bamsdall, OK	0.4	—	0.4
Petrolite Bareco Div, Kilgore, TX	—	0.3	0.3
Petrowax PA, Emleton, PA	0.9	0.1	1.0
Petrowax PA, Smethport, PA	1.0	0.2	1.2
Quaker State, Newell, WVA	—	0.5	0.5
Shell Oil, Deer Park, TX	1.0	—	1.0
Star Enterprise, Port Arthur, TX	—	1.8	1.8
Sun Company, Tulsa, OK	0.8	—	0.8
Sun Company, Yabucoa, Puerto Rico	—	2.1	2.1
Unocal Corporation, Rodeo, CA	0.7	0.3	1.0
Witco Chemical, Bradford, PA	—	0.5	0.5
Total	12.6	14.9	27.5

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Table 1.7 Canadian Lube and Wax Capacities—January 1, 1993

Refiner	Capacity, 1000 BPCD				Percent of crude	
	Crude	Base oil	Wax	Total	Base oil	Wax
Imperial Canada	281.0	8.4	2.8	11.2	3.0	1.0
Petro Canada	41.5	4.9	1.0	5.9	11.8	2.4
Shell Canada	28.0	2.7	1.3	4.0	9.6	4.6
International Waxes Canada	—	—	1.0	1.0	NA	NA
Total Canada	350.5	16.0	6.1	22.1	4.6	1.7

Prepared from the 1993 NPRA Survey, by permission of the NPRA.

Table 1.8 U.S. Base Oil and Wax Capacity Trends: 1976–1993

	Base oil capacity, MBPCD			Wax capacity, MBPCD			
Year	Paraffin	Naphthene	Total	Finished	Other	Total	Crude MBPCD
1976	—	—	227.6	12.3	11.8	24.1	4753.8
1977	—	—	226.9	13.1	12.1	25.2	5200.7
1978	163.3	63.8	227.1	13.0	16.7	26.7	5486.6
1979	166.8	61.5	228.3	13.1	15.8	28.9	5467.5
1980	169.3	60.3	229.6	12.9	16.2	29.1	5405.8
1981	176.9	59.3	227.6	13.6	15.9	29.5	5413.7
1982	170.7	64.4	235.1	12.6	16.3	28.9	5320.9
1983	169.1	64.9	233.8	13.7	15.5	29.1	5133.9
1984	169.0	66.8	235.8	13.6	15.7	29.3	5002.0
1985	166.6	66.5	233.1	12.3	15.8	28.1	4854.9
1986	163.3	64.4	227.7	11.9	15.4	27.3	4865.3
1987	162.3	65.9	228.3	12.0	15.3	27.3	4862.4
1988	166.4	57.1	224.5	12.5	15.6	28.1	4836.2
1989	164.6	65.6	230.2	12.3	15.2	27.5	4766.9
1990	163.8	62.5	226.3	12.0	19.4	31.2	4533.7
1991	161.4	59.5	220.9	11.3	17.2	28.5	4119.6
1992	160.9	50.0	210.9	12.8	18.2	31.0	4184.6
1993	150.3	53.1	203.4	12.6	14.9	27.5	3876.7

Prepared from Ref. [9] by permission of the NPRA.

Table 1.9 Leading Lube and Wax Manufacturers in the USA

Year	1979	1981	1983	1985	1987	1989	1991	1993
No. Lube Plants	44	40	37	38	36	35	29	27
No. Wax Plants	34	33	33	29	28	26	22	21
No. Refiners	30	27	26	26	24	24	23	21
Leading Refiners	MBPCD							
Exxon	49.4	50.2	51.5	53.3	52.8	51.0	51.0	48.4
Sun Oil	32.8	33.9	33.8	26.5	27.0	29.2	29.4	19.2
Chevron/Gulf	22.2	22.2	18.0	26.3	22.3	23.0	22.1	10.0
Star/Texaco	22.8	21.9	21.9	16.5	17.9	18.5	18.2	18.2
Shell Oil	18.4	18.4	19.6	19.7	15.6	19.6	18.5	19.4
Mobil Oil	17.7	18.8	18.2	18.3	16.1	18.3	19.8	19.9
Pennzoil	7.9	6.3	14.1	14.1	14.3	14.2	16.7	16.5
Percent of total	66.9	66.8	67.0	66.7	65.2	67.7	70.4	65.2
For the top five	56.6	57.2	55.2	55.2	53.2	54.8	56.5	55.0

Prepared from Ref. [9] by permission of the NPRA.

Table 1.10 U.S. Base Oil and Wax Processing Profile, January 1, 1993

Process	Capacity Capacity MBPCD	Capacity as percent of Crude	Capacity as percent of Base Oil
Crude	3648.7	100.00	179,3.9
Base oil	203.4	5.57	100.0
Wax	27.5	0.75	13.5
Deasphalting	59.0	1.61	29.0
Solvent refining	308.3	8.45	151.6
Hydrogen refining	87.7	2.41	43.1
Dewaxing	193.4	5.30	95.1
Lube finishing	133.1	3.63	65.5
Wax finishing	8.5	0.23	4.2
Total all processes	790.0	21.65	388.4

Prepared from the 1993 NPRA Survey by permission of the NPRA.

VII. SUPPLY AND DEMAND OF LUBRICANT BASE OILS [7,8,10,11]

Recent reports concerning the supply and demand of lubricant base oils have been presented at the Annual Meetings of the National Petroleum Refiners Association [7,8,10,11]. These reports indicate that the current base oil supply exceeds the demand and that an overall shortage of worldwide base oil supply is expected in about 1997.

Although there is an overall surplus of base oil supply on a worldwide basis, there are regions where a shortage of base oils exist. These demands are currently being made by importing base oils into regions of shortages. Summaries of the lubricant base oil demand and supply forecasts through the year 2010 are presented in Tables 1.11–1.13 [7]. It should be noted that these forecasts do not include unforeseen happenings such as debottlenecking of existing facilities, new base oil plants and political and economic events which may increase or decrease the supply and demand of waxes and lubricants. In addition, changes in the specifications, such as decreased volatility requirements and better cold temperature properties may lead to an increased use of synthetics or a shortage in some grades of base oils and a surplus in some other grades.

The reader is referred to references [7,8,10,11] and other published reports for additional information on base oil supply and demand under different economic forecasts.

Table 1.11 1989–2005 Base Oil Demand Forecast (Million Barrels)

Region	1989	1990	1995	2000	2005
North America	59.2	57.8	57.2	58.5	59.1
Other Americas	17.2	17.8	20.3	22.7	24.5
W. Europe	38.4	39.4	40.7	42.0	43.2
Australia/Asia	31.7	32.7	37.8	43.6	50.4
Middle East/Africa	17.1	17.7	19.7	21.7	24.3
Central/ E. Europe	10.6	10.0	9.5	9.5	9.5
China	12.1	12.0	13.8	15.0	16.5
Former USSR	58.2	57.9	55.1	54.3	54.8
Free World	163.6	165.4	175.7	188.5	201.5
Total World	244.5	245.3	254.1	267.3	282.3

Prepared from Ref. [7] by courtesy of Texaco, Inc.

Table 1.12 Estimated Base Oil Manufacturing Capacity (Million Barrels)

Region	1890	1990	1995	2000	2005
North America	72.5	70.6	64.7	64.7	64.7
Other Americas	16.9	16.9	18.5	18.5	18.5
W. Europe	42.7	42.7	42.7	42.7	42.7
Australia/Asia	31.3	31.5	34.6	36.0	36.0
Middle East/Africa	11.3	11.3	15.2	15.2	15.2
Central/ E. Europe	9.9	9.9	11.0	11.0	11.0
China	13.3	13.3	15.2	16.4	17.9
Former USSR	58.5	58.5	55.3	55.5	55.5
Free World	174.7	173.0	175.7	177.1	177.1
Total World	256.4	254.7	257.4	260.0	261.5

Prepared from Ref. [7] by courtesy of Texaco, Inc.

Table 1.13 Surplus/(Shortage) Lube Base Oils (Million Barrels)

Region	1990	1995	2000	2005	2010
North America	13.3	7.5	7.5	6.2	5.5
Other Americas	(0.3)	(0.9)	(1.7)	(4.2)	(5.9)
W. Europe	4.3	3.3	2.0	0.7	(0.5)
Australia/Asia	(0.4)	(1.2)	(3.2)	(7.7)	(14.4)
Middle East/Africa	(5.8)	(6.4)	(4.5)	(6.4)	(9.1)
Central/ E. Europe	(0.7)	(0.2)	1.5	1.6	1.6
China	1.2	1.3	1.4	1.4	1.5
Former USSR	0.3	0.5	0.4	1.2	0.7
Free World	11.1	7.6	0.1	(11.4)	(24.3)
Total World	11.9	9.2	3.4	(7.2)	(20.5)

Prepared from Ref. [7] by courtesy of Texaco, Inc.

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2

Crude Oils, Base Oils, and Petroleum Wax

I. CRUDE OILS: COMPOSITION

Crude oils are the source of the feedstocks used to manufacture lubricant base oils, waxes and the hydrocarbons used in the manufacture of synthetic oils. Crude oils contain considerable quantities of carbon and hydrogen and small amounts of sulfur, oxygen, nitrogen and inorganic salts and relatively smaller quantities of metals. Although the physical properties of crude oils vary widely, their composition usually falls in the ranges shown in Table 2.1.

The major types of hydrocarbons present in crude oils consist of 1) normal paraffins, 2) branched paraffins (iso-paraffins), 3) cycloparaffins (naphthenes) and 4) aromatics. The hydrocarbons found in lubricant base oils consist of paraffins, isoparaffins, naphthenes and aromatics containing about 15 or more carbon atoms.

Table 2.1 Composition of Crude Oils

Component	Wt %	Component	Wt %
Carbon	83–87	Hydrogen	11–14
Sulfur	0–3	Nitrogen	0–1
Oxygen	0–0.5	Metals	0–0.2

A. Normal Paraffins

Normal paraffins consist of carbon atoms connected by a single carbon to carbon bond. All other bonds are saturated with hydrogen atoms; ethane, butane and hexane depicted in Figure 2.1 are examples of normal paraffins. The paraffins are characterized by the fact that the carbon atoms are connected by a single carbon to carbon bond and the bonds not thus connected are connected to a hydrogen atom. The general formula for paraffin series of hydrocarbons is C_nH_{2n+2}; where n refers to the number of carbon atoms in the molecule.

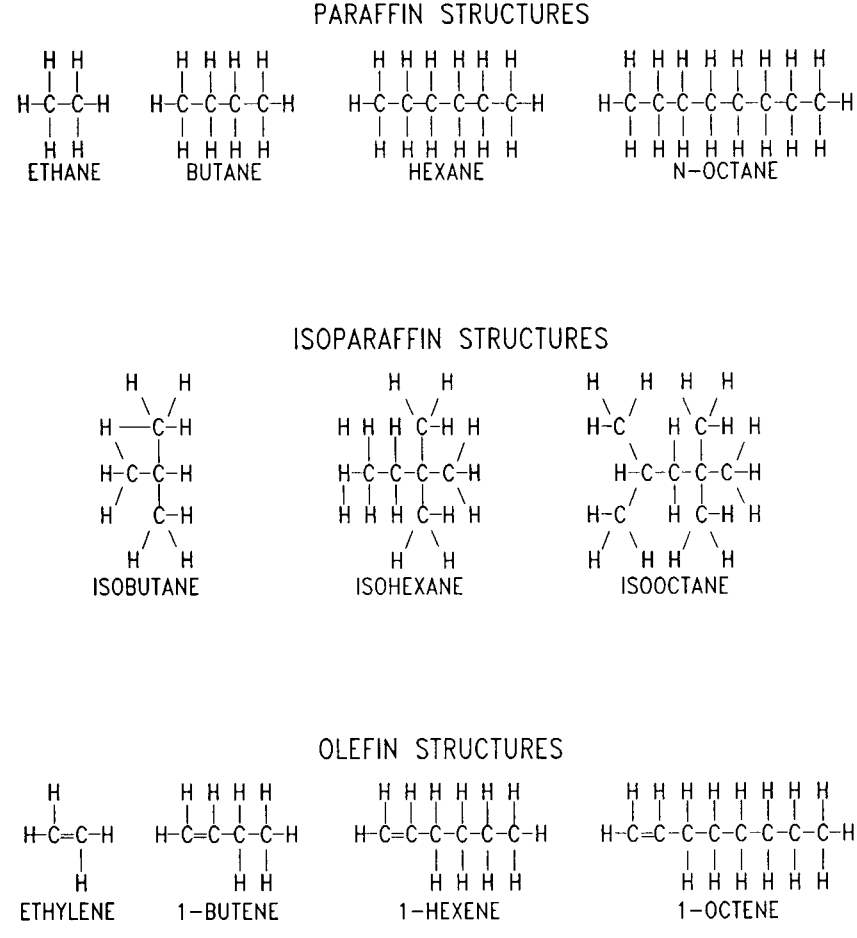

Figure 2.1 Simple paraffin, isoparaffin, and olefin hydrocarbon structures.

B. Iso-Paraffins

Iso-paraffins are paraffinic hydrocarbons which contain the same number of carbon and hydrogen atoms as the normal paraffins; these compounds have different molecular structures and properties. These different compounds are called isomers and arise from the fact that carbon atoms can be joined in more than single branched chains as depicted in Figure 2.1.

The number of isomers increase geometrically with an increase in carbon number. For example there are two isomers of butane, three of pentane, eight of hexane, 17 of octane and 4347 for the smallest lube molecule containing 15 carbon atoms [1].

C. Cycloparaffins

Cycloparaffins, normally called naphthenes, consist of carbon atoms bonded to form a ring such as that of cyclohexane in Figure 2.2. All non carbon to carbon bonds are saturated with hydrogen. There are many different types of

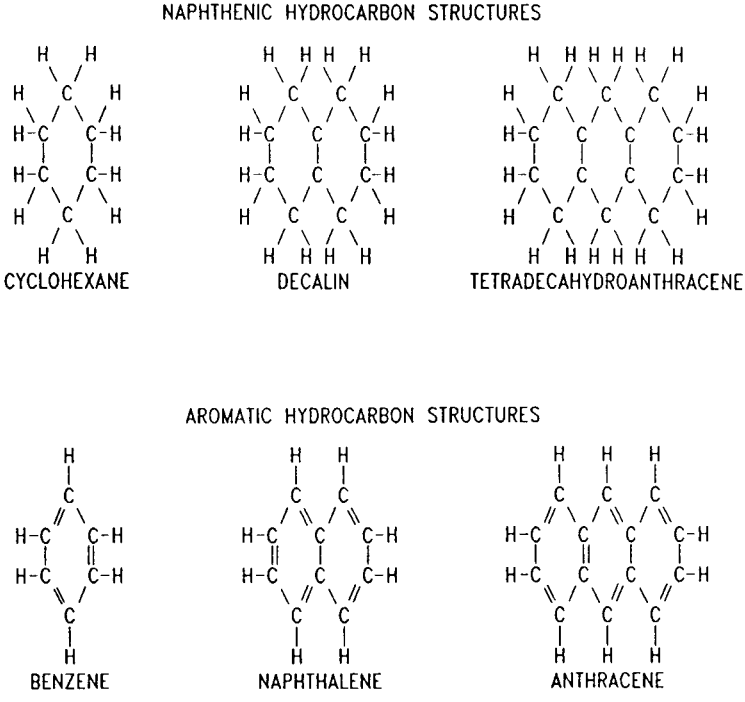

Figure 2.2 Simple naphthenic and aromatic hydrocarbon structures.

naphthenes present in crude oils. With the exception of cyclopentane, methylcyclopentane, cyclohexane, cycloheptane and the xylenes, most are generally not considered as individual hydrocarbons. The naphthenes are generally classified by their boiling range and properties. Many of the naphthenes present in crude oils also contain normal paraffin or isoparaffin side chains bonded to one or more of the carbon atoms of the naphthene ring.

D. Olefins

Olefins are very similar to paraffins in structure but contain at least one double bond between two adjacent carbon atoms. Olefins are not normally found in crude oils; they are formed during processing. Diolefins are also formed during processing, but react very quickly to form high-molecular weight polymers. Olefins are undesirable in finished lubricants because they are reactive and are easily oxidized and polymerized.

The structures of ethylene, n-butene and n-hexene are depicted in Figure 2.1. The general formula for the olefin series is C_nH_{2n}; where n is the number of carbon atoms in the molecule.

E. Aromatics

Aromatic hydrocarbons contain a benzene ring, six carbon atoms bonded to form a ring which is unsaturated; that is, they are deficient in hydrogen. Aromatics are very stable and frequently behave as a saturated compound; this is particularity true of aromatics which contain paraffin or isoparaffin side chains in place of hydrogen attached to the ring carbons. These mixed structures have physical and chemical properties of both paraffins and aromatics and are classified according to the cyclic compound. Figure 2.2 presents the structures of some simple aromatic compounds and Figure 2.3 presents the structure of some aromatic compounds found in base oil feedstocks. Many of the aromatics contain normal paraffin, isoparaffin, naphthene structures as side chains attached to a carbon atom in the aromatic ring; these side chains and hydrogen have been omitted for the aromatics shown in Figure 2.3.

It should be noted that the hydrocarbons containing less than about 15 carbon atoms are not present in lubricant base oils or in the feedstocks used to make these base oils. The reason they are not present is that they have low boiling points—high volatility, low flash and fire points and low viscosity. In addition, the normal paraffins and waxy isoparaffins, waxy naphthenes and waxy aromatics are removed as wax during processing. Many of the aromatics are removed by deasphalting and solvent extraction or converted to naphthenes and isoparaffins using severe hydrogenation processes.

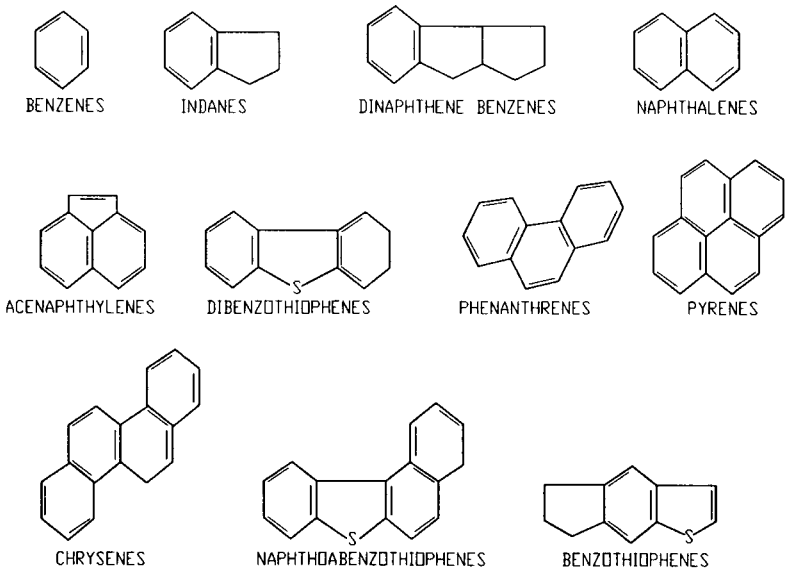

Figure 2.3 Structure of aromatic components in lube feedstocks.

F. Asphaltenes and Resins

Asphaltenes and resins are also aromatics which are found in crude oils. These materials are most often found in the residua or very heavy vacuum gas oils and consist of materials classified as asphaltics. Asphaltenes are generally defined as the pentane insoluble or heptane insoluble hydrocarbons and the resins are the materials dissolved in these solvents. Although other solvents can be used, pentane and heptane are most commonly used. Asphaltic materials can be further separated into other components such as 1) asphaltenes which are soluble in n-pentane or n-heptane but insoluble in benzene, 2) carbenes; the n-pentane or n-heptane insoluble materials which are insoluble in benzene but soluble in carbon disulfide and 3) carboids; the n-pentane or n-heptane insoluble materials which are insoluble in benzene, carbon disulfide and other organic solvents [2, 3]. Carboids are seldom found in crude oils but are the products of thermal decomposition and cracking [2].

Resins are the pentane- or heptane-soluble materials which are removed from solution on percolation through clays such as fullers earth or alumina [1,3]. A summary of the classifications based on separation using solvents is presented below.

Classification of Asphaltic Materials by Solubility

Solvent	Carboids	Carbenes	Asphaltenes	Resins
Pentane or heptane	Insoluble	Insoluble	Insoluble	Soluble
Benzene	Insoluble	Insoluble	Soluble	Soluble
Carbon disulfide	Insoluble	Soluble	Soluble	Soluble

G. Sulfur, Nitrogen and Oxygen

Sulfur, nitrogen, oxygen and some metals are also found in crude oils. Sulfur, nitrogen and oxygen are usually found in place of carbon or hydrogen in the structure of the different hydrocarbon types. The small amounts of metals are generally found in the higher molecular weight (and higher boiling) compounds found in crude oils.

H. Metallic Constituents [3]

The metals present in petroleum are of interest to petroleum refiners because they lead to ash deposits and affect the activity of catalysts used in downstream processing. Small quantities of metals are usually present in crude oils. They are usually present as water soluble salts which are removed by desalting. Although some of the metallic compounds are volatilized during distillation, the majority of the metals are concentrated in the residua. These metallic compounds can be removed by light hydrocarbon solvents of the type used in deasphalting processes. The concentration of some metals present in crude oils is presented in Table 2.2 [3].

Table 2.2 Ranges of Principle Trace Elements in Petroleum

Metal	Concentration, ppm	Metal	Concentration, ppm
Copper	0.2–12.0	Gallium	0.001–0.1
Calcium	1.0–2.5	Titanium	0.001–0.4
Magnesium	1.0–2.5	Zirconium	0.001–0.4
Barium	0.001–0.1	Silicon	0.1–5.0
Strontium	0.001–0.1	Tin	0.1–0.3
Zinc	0.05–1.0	Lead	0.001–0.2
Mercury	0.03–0.1	Vanadium	5.0–1500
Cesium	0.001–0.6	Iron[a]	0.04–120.0
Boron	0.001–0.1	Cobalt	0.001–12.0
Aluminum	0.5–1.0	Nickel	3.0–120.0

[a] May be due to contamination with iron containing equipment Reprinted from Ref. [3], p. 248.

II. CLASSIFICATION OF CRUDE OILS

The U.S. Bureau of Mines system classifies crude oils according to the API gravity of two key fractions obtained by distillation as summarized in Table 2.3 [4,5].

Although the U.S. Bureau of Mines has developed the system shown in Table 2.3 for the classification of crude oils, one finds that refiners usually classify a crude oil as (1) paraffin base, (2) naphthene base (3) mixed base or (4) asphalt base; Although there appears to be no specific definition for these classifications, Table 2.4 provides statements concerning the general definitions for these classifications and the suitability of crude oils for base oil and wax manufacture. There are crudes which can be classified in each of the categories and which are avoided by a single or all base oil and wax refiners for one particular reason or another. The main reason for rejecting a crude is not being able to manufacture the desired qualities and quantities of products with the process facilities available to the refiner.

III. CRUDE OIL PROPERTIES

Crude oils are very complex and, except for the low boiling components, no reported attempt has been made by the refiner to analyze for the pure components present in crude oils. The results of relatively simple tests are used with correlations to evaluate crude oils as feed for a particular refinery. The evaluation of crude oils for use in base oil and wax manufacture are consider-

Table 2.3 U.S. Bureau of Mines Classification of Crude Oils

	API Gravity of Fraction	
Key Fraction	Number one	Number two
Boiling range, °C	250–275 (482–527)	275–300 (736–786)
Pressure, mm Hg	760	40 760
Classification		
Paraffin	40 or lighter	30 or lighter
Paraffin, intermediate	40 or lighter	20.1–29.9
Intermediate, paraffin	33.1–39.9	30 and lower
Intermediate	33.1–39.9	20–30
Intermediate, naphthene	33.1–39.9	20 or heavier
Naphthene, intermediate	33 or heavier	20.1–29.9
Naphthene	33 or heavier	20 or heavier
Paraffin, naphthene	40 or lighter	20 or heavier
Naphthene, paraffin	33 or heavier	30 or lighter

Reprinted from Ref. [5].

Table 2.4 General Classification of Crude Oils

Paraffin base crude oils
Contain little or no asphalt
Contain varying amounts of wax
Suitable for wax manufacture
Suitable for solvent neutral oil manufacture
Naphthene base crude oils
Contain little or no asphalt
Contain little or no wax
Suitable for naphthene pale oil manufacture
Preferred for speciality oils manufacture
Not suitable for solvent neutral oil manufacture
Mixed base crude oils
Contain wax and asphalt
Suitable for base oil manufacture
Low yield of base oils
Asphalt base crude oils
Residue primarily asphaltic
High sulfur and nitrogen contents
Suitable for base oil manufacture

ably more complex than those used by a fuels refinery and involve process studies using the lube processes available to the refiner. The more useful properties of a crude oil are summarized in Table 2.5.

In addition to having different physical and chemical properties, crude oils contain different quantities of hydrocarbons within a given boiling range. Figure 2.4 presents the boiling range distribution for three crude oils.

IV. REFINERY PRODUCTS

Although several thousand products are made from or derived from petroleum, the major refinery products distilled from crude oils are listed in Table 2.6.

V. CRUDE EVALUATION METHODS

Since crude oils vary widely in composition and their suitability for lube manufacture cannot be determined from the assays normally used to evaluate the properties of a crude oil, refiners have developed proprietary screening and evaluation methods which are specific to their operations to assess the suitability of crude oils for lube manufacture [3,6,7]. These methods range from simple distillations for inspection testing of distillates and residua to processing

Table 2.5 Properties of Crude Oils

API gravity	~10–50 High gravity is most valuable
Sulfur, wt %	~0.1–5 Low sulfur is most desirable
Nitrogen, wt %	~0.1–2 Catalyst poison
Oxygen content, wt %	~0.1–0.5 Corrosion problems
Pour point, °F	Related to wax content
Carbon residue, wt %	Related to asphalt content High content is less valuable
Salt content	Depends on crude source High content: corrosion
Characterization factor ~10–15 Watson K =	$\frac{(\text{Average BP, °R})^{0.5}}{\text{Specific gravity}}$
Metals content, PPM	~2–1000 Affects catalyst life and activity: low content preferred
Distillation range	Depends on crude oil indicates product quantities

(deasphalting, extraction and dewaxing) studies that establish yields of desired base oils. Those crudes showing promise are further processed in large pilot plants or in plant trials to prepare large quantities of base oils for product formulation and detailed quality evaluation.

Two of the methods that are used by Texaco consist of atmospheric and vacuum fractionation to prepare vacuum distillates and residual oils for further processing [8,9]. In one screening type evaluation the distillates and residua are batch processed to determine potential yields and quality of base oil present in the crude oil. A second method consists of atmospherically fractionating the crude followed by vacuum fractionation of the reduced crude into narrow distillate cuts in the range of 45 SUS at 100°F to 200 SUS at 210°F and a vacuum residuum. The narrow cuts are used to blend the feedstocks corresponding to those to be manufactured. An example for preparing three distillates and a long residuum for pilot plant processing is presented in Table 2.7 [9]. The data developed on the crude, residua and distillate blends are listed in Table 2.8 [9].

Processing conducted on these feedstocks consist of propane deasphalting, solvent refining and solvent dewaxing. In some cases catalytic dewaxing and hydrogen finishing are conducted to prepare base oils for quality evaluation.

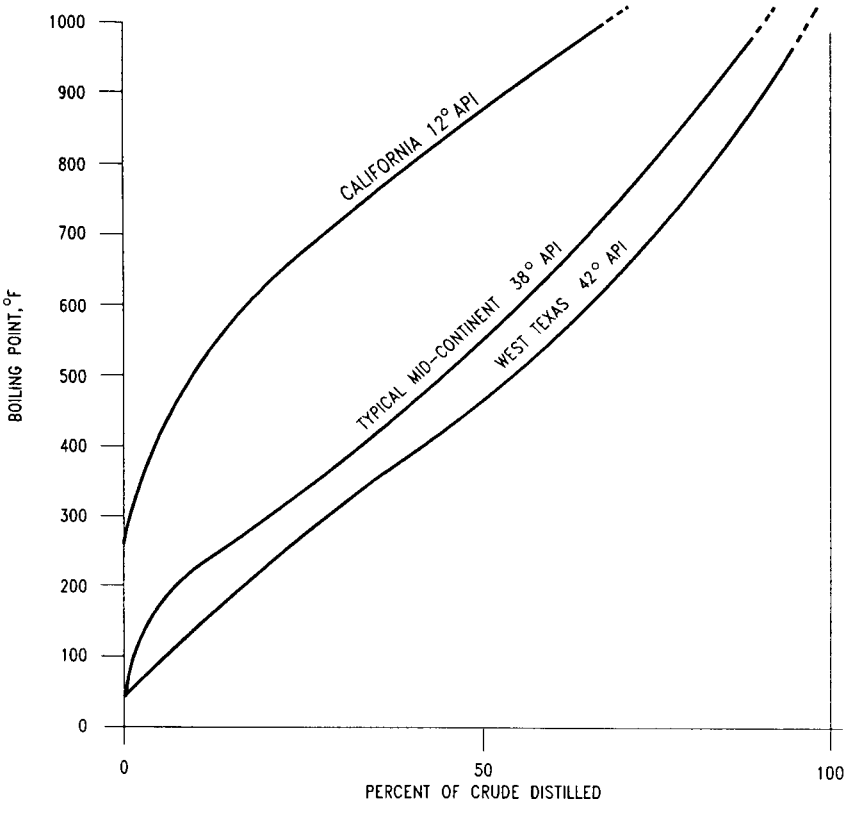

Figure 2.4 Boiling ranges for some crude oils.

Table 2.6 Crude Distillation Products

Products	Uses
Methane	Fuel and hydrogen production
Ethane	Fuel and petrochemical feedstock
Propane	Fuel and petrochemical feedstock
Butane	LPG and petrochemical feedstock
LSR gasoline	Blending stock and further processing
Naphtha	Blending stock and further processing
Middle distillates	Kerosene, diesel, jet fuel and heating oil
Light and heavy gas oils	Fuel oil and other products
Light and heavy VGO's	Other processing
Lube distillates	Lube processing
Vacuum residuum	Fuel oil, asphalt, coke, feedstock to fuel and lube manufacturing processes

Table 2.7 Blending of Distillates and Long Residuum

Feedstock	Viscosity	Flash Point
Spindle Distillate	80–90 SUS @ 100°F	360°F
Light Distillate	175–200 SUS @ 100°F	400°F
Heavy Distillate	80–90 SUS @ 210°F	490°F
Long Residuum	Nominal 1000+ °F cut point	

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The process conditions used vary according to the feedstock being used and the base oil to be manufactured. A range of typical solvent refining conditions is summarized in Table 2.9. Specific conditions depend on the solvent being used and the expected performance of the vacuum distillates. Solvent dewaxing is done by batch dewaxing procedures using high solvent-to-oil ratios and filtration at temperatures which will provide base oils of the desired pour point. In those cases in which design data are desired, special simulations of commercial operations are conducted to provided the needed design data.

Table 2.8 Data Obtained on Crude, Distillates and Residua

	Residuum			
	Crude	Atmos.	Vac.	Distillates
Yield basis crude, vol %		X	X	X
Position in crude, vol %		X	X	X
Tests				
API gravity	X	X	X	X
Two viscosities	X	X	X	X
Viscosity index		X	X	X
Pour point, °F	X	X	X	X
ASTM color				X
Conradson carbon, wt %	X	X	X	X
Flash, COC°F		X	X	X
Sulfur, wt %	X	X	X	X
Refractive index, 70°C	X	X	X	X
Basic nitrogen	X	X	X	X
Total nitrogen	X	X	X	X
Neutralization no.	X	X	X	X
Oil content				X
Wax content				X
True boiling point by GC	X	X		X

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Table 2.9 Continuous Solvent Refining of Distillates

Continuous Refining	Spindle	Light neutral	Heavy neutral	Deasphalted oil
Solvent dosage, vol %	100–400	100–400	100–400	100–450
Raffinate out temp, °F	110–200	140–220	160–240	160–210
Extract out, temp, °F	100–170	130–190	150–210	150–190

Inspection tests obtained on the products, intermediate products and by-product streams depend on the yield and quality of the intermediate streams and dewaxed oils. Table 2.10 lists some of the information and tests that are obtained in a preliminary evaluation [9].

The extensive data developed during this type of evaluation are used to prepare about 15 tables and 20 figures. Table 2.11 lists some of the figures developed from the process data and inspection tests [9] on the crude, feedstocks and base oils.

When larger quantities of base oils and by-products are required for quality evaluation which may include bench as well as field testing or qualification testing, base oils will often be obtained from plant trials. This type of testing may, in some cases, take a year or two to complete.

VI. BASE OIL TYPES AND PROPERTIES [10]

Since the physical properties and chemical compositions of lube fractions from different crudes vary widely, the refiner must vary the processing conditions or use different processing sequences to meet product specifications; even so, the base oils will vary in chemical composition or ratio of the different hydrocar-

Table 2.10 Types of Data Developed on Products and By-Products from Processing Studies

Refining temperature	Refining dosage
API gravity	Refractive index
Two viscosities	Oil content
Viscosity index	Wax content
Pour point	Flash, COC°F
ASTM color	Clay gel analysis
Ash content	Volatiles
Conradson carbon	Solvent content
Sulfur content	Nitrogen content

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Table 2.11 Crude Evaluation Figures

Cut flash versus position in crude
Cut viscosity versus position In crude
Gravity versus cut mid-boiling point
Viscosity versus cut flash point
Change in viscosity across refining
Change in gravity across refining
Refining response of distillates
Refining response of deasphalted oils
Dewaxed oil yield of raffinates
Waxy oil RI versus dewaxed oil VI
Change in viscosity across dewaxing
Change in gravity across dewaxing

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bon types. A summary of the more important properties of the various base oil components is shown in Table 2.12.

The preferred compounds for the manufacture of base oils are the isoparaffins of high VI and low pour point. The normal paraffins are the highest in VI but they are undesirable because they have very high pour (solid) points. Some isoparaffins, naphthenes and aromatics also have high pour points and are undesirable as lube base oils. Aromatics generally have the lowest VI and oxidative stability. Naphthenes generally have intermediate VI's and very low pour points which make them useful in the manufacture of speciality lubricants. Table 2.13 presents the viscosity index of the hydrocarbon types separated from a hydrocracked base oil by Nippon Oil [11].

A. Types of Lubricating Oil Stocks

Mineral base oils are of two types, the conventional base oils which have viscosity indices of 95 or less and non-conventional base oils with viscosity indices above 100. The conventional base oils are manufactured using the sol-

Table 2.12 Base Oil Component Properties

Component	n-Paraffin	Iso-paraffina	Naphthene	Aromatic
Viscosity index	High	High	Medium	Low
Pour point	High	Low	Low	Low
Oxidative stability	Good	Good	Fair	Poor
Thermal stability	Good	Good	Fair	Poor

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Table 2.13 Viscosity Index of Hydrocarbons

Hydrocarbon type	Viscosity index
Normal paraffins	175
Iso-paraffins	155
Mononaphthenes	142
Dinaphthenes	70
Aromatics	50

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vent refining processes and non-conventional base oils are usually manufactured using severe hydrogen refining processes or from the isomerization of wax, high wax content feedstocks or from lube fractions from selected crude oils.

1. Conventional Base Oils

Conventional base oils consist of two types, those that are highly paraffinic and those that are highly naphthenic as defined by their naturally occurring viscosity index and pour point. Table 2.14 presents a comparison of a paraffinic and a naphthenic feedstock, raffinate and base oil [10].

These data show (1) that naphthene-based feedstocks exhibit low VI and pour points and (2) that the paraffin-based feedstocks exhibit high VI and high

Table 2.14 Comparison of Naphthenic (NPO) and Paraffinic (SNO) Base Oils[a]

	Distillate		Raffinate		Base oil	
Property	NPO-100	SNO-100	NPO-100	SNO-100	NPO-100	SNO-100
API gravity	23.0	26.7	28.8	34.7	28.8	32.4
COC flash, °F	355	380	355	380	355	380
Pour point, °F	−35	75	−20	85	−20	0
Visc SUS @ 100 °F	108	103	100	85.1	100	100
Viscosity index	17	86	61	110	61	95
ASTM color	7	4.5	1.5	1.5	L0.5	L0.5
Sulfur, wt %	0.10	1.1	0.03	0.39	0.02	0.17
Aromatics, wt %	34	34	24	17	24	16

[a] The SNO-100 base oil is the SNO-100 raffinate after dewaxing and hydrofinishing. The NPO-100 base oil is the hydrofinished raffinate.

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pour; naphthene feedstocks are essentially wax free and paraffinic feedstocks must be dewaxed because they contain wax.

Mineral base oils used in the manufacture of lubricants include (1) solvent neutral oils (SNO), naphthene pale oils (NPO), bright stocks (BS), cylinder oils (CO) and speciality oils.

2. Neutral or Solvent Neutral Oils

Solvent neutral oils (SNOs) are vacuum-distilled paraffinic base oils that are refined for VI appreciation and aromatics removal; they are dewaxed for pour point reduction, and hydrogenated for stability. These base oils are characterized by high API gravity, flash point, aniline point and VI.

A comparison of some base oil feedstocks used to manufacture SNO 335 are shown in Table 2.15 [10]. These data show that the composition of the solvent neutral oils produced will vary both before and after processing as a result of using different crude oils. The data also show the effect of solvent extraction on the aromatic and sulfur contents of the refined oils [10].

3. Bright Stocks and Cylinder Oils

Bright stocks and cylinder oils are residual base oils manufactured from paraffinic and naphthenic vacuum residua. Bright stocks are made using propane deasphalting, solvent extraction or hydrogen refining, and catalytic or solvent dewaxing. Cylinder oils are manufactured using propane deasphalting with solvent dewaxing sometimes used to reduce pour point. Test results for some SNOs, a bright stock and a cylinder oil are shown in Table 2.16 [10].

4. Naphthene Pale Oils

Naphthene pale oils (NPOs) are vacuum-distilled naphthenic base oils that are refined for aromatics removal, and dewaxing is generally not required. Test results for two solvent extracted and two hydrofinished naphthenes manufac-

Table 2.15 Comparison of 335 Neutral Feedstocks 90 VI at 10 °F Pour Point Oil

	Aromatics wt%		Sulfur wt%	
Crude Source	Raw	Refined	Raw	Refined
U.S. coastal A	31.7	16.5	0.26	0.10
U.S. coastal B	35.9	12.8	0.32	0.09
West Texas A	30.2	14.3	0.47	0.21
West Texas B	47.5	NA	1.75	0.68
Mid east A	40.5	25.6	1.45	0.53
Mid east B	53.4	29.9	2.05	0.76
Mid east C	54.4	37.4	2.31	1.09

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Table 2.16 SNOS, Bright Stock and Cylinder Oil

Property	SNO-100	SNO-150	SNO-320	SNO-850	BS-150	Cyl. Oil
API gravity	32.4	30.9	29.3	26.8	26.5	20.4
COC flash, °F	380	404	440	505	545	585
Pour point, °F	10	5	10	15	10	20
Visc SUS @ 100°F	107	155	332	844	2586	9440
Viscosity index	95	96	97	89	95	70
ASTM color	0.5	0.5	L1.5	2.5	L4.5	8+
Carbon resid. wt %	0.02	0.02	0.03	0.11	0.65	2.90
Sulfur, wt %	0.14	0.27	0.31	0.38	0.52	0.70
Aromatics, wt %	16.1	23.4	25.4	27.6	32.5	36.6

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tured from a U.S. Coastal Crude Oil are shown in Table 2.17. These data show that the solvent-extracted NPOs are more paraffinic than the hydrofinished NPOs. The solvent refined NPOs have lower aromatic and sulfur contents and higher API gravity, VI and pour point than the mildly hydrofinished oils. However, it should be noted that severe hydrogen refining of the feedstocks would result in the manufacture of technical and pharmaceutical grade white oils from either selected distillates or solvent extracted NPOs. NPOs produced from Californian and Venezuelan crude oils using the same processing sequence and severity will contain higher aromatic and sulfur contents than those shown in Table 2.17.

Table 2.18 presents data which show the variations in sulfur and aromatic content, viscosity index and pour of some commercially available NPO 100 oils [10].

Table 2.17 Comparison of Solvent Extracted and Hydrotreated Naphthene Pale Oils

Processing	NPO-100 Hydrogen	NPO-100 Solvent	NPO-900 Hydrogen	NPO-900 Solvent
API gravity	26.0	28.8	22.2	24.9
COC flash, °F	320	355	430	430
Pour point, °F	−40	−20	−5	10
Visc. SUS @ 100°F	107	103	916	901
Viscosity index	34	61	38	66
ASTM color	1.0	L0.5	2.5	L2.5
Sulfur, wt %	0.07	0.02	0.10	0.05
D2007 Arom., wt %	35	24	27	23

Table 2.18 Comparison of Some Naphthene Pale Oil 100

	Sulfur, wt %	Aromatics, wt %	Visc. index	Pour, °F
NPO A	0.06	25.6	20	−50
NPO B	0.02	31.9	−7	−60
NPO C	0.07	31.8	34	−40
NPO D	0.02	24.0	61	−20

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B. Composition of Base Oils

A comparison of the compositions of several 100 neutrals of about the same VI and pour point made from different crude sources using various processing sequences is shown in Table 2.19. The data show that 100 neutral base oils vary widely in chemical composition. Although the severely hydrotreated base oils have low aromatic, sulfur and nitrogen contents; it should be noted that base oil D is also low in sulfur and aromatics. This oil was manufactured by solvent refining and solvent dewaxing; no finishing was used. base oil E was manufactured in a similar manner using a different crude source; it contains considerably more sulfur and aromatics than base oil D. It should be noted that some of the high aromatic content oils were hydrofinished more severely than others; this is exemplified by the sulfur content of base oils F and G and I and J.

Table 2.19 Composition of Some Commercial 95-105 VI SNO's-100

		Wt %			
	Processing	Sulfur	Aromatics	Paraffins	Naphthenes
Base oil A	HC-SD-HR	0.002	4.50	25.60	69.90
Base oil B	HC-CD-HR	0.002	5.60	23.50	70.90
Base oil C	HC-SD-SR	0.010	7.60	20.70	71.70
Base oil D	SR-SD	0.050	9.30	18.80	71.90
Base oil E	SR-SD	0.740	28.90	25.00	46.10
Base oil F	SR-HF-SD	0.550	29.80	25.20	45.00
Base oil G	SR-HF-SD	0.366	28.10	19.50	52.40
Base oil H	SR-HF-SD	0.256	23.60	19.60	56.80
Base oil I	SR-CD-HF	0.590	27.20	24.30	48.50
Base oil J	SR-CD-HF	0.240	27.00	20.50	52.50

CD = Cat dewaxing HC = Hydrocracking HF = Hydrogen finish
SD = Solvent dewax HR = Hydrogen refine SR = solvent refining

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Table 2.20 Comparison of SNO 100 Lube Base Oils

Property	PAO[a]	VHVI[b]	HVI[c]	Conventional
Viscosity index	125–127	130–145	109–129	95–105
Pour point, °F	−50	0 to 20	0 to 20	0 to 20
Sulfur, wt %	Nil	Nil-0.10	Nil-0.20	Nil-0.75
Aromatics, wt %	Nil	1–10	6–15	4–30
Naphthenes, wt %	Nil	10–25	20–60	45–72
Paraffins, wt %	100	70–85	25–75	15–65
Cold crank sim. Cp@25°C	500–1400	1400–1600	1400–3500	1300–5000
Noack volatility, %	11–12	12–14	16–22	18–35
Thermal stability	Excellent	Excellent	Very good	Good
Oxidation stability	Excellent	Excellent	Very good	Good
Additive solubility	Very good	Very good	Excellent	Excellent

[a] PAO = Polyalphaolefin
[b] VHVI = Very High VI
[c] HVI = High VI
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Table 2.20 provides a comparison of some major properties for some non-conventional base oils with conventional oils. These data show that it is not always possible to differentiate between the properties of the oils and their performance in special tests.

The composition of solvent and catalytically (ZSM-5) dewaxed oils is compared in Table 2.21 [12]. These data show that light neutral feedstocks and dewaxed oils have a higher normal paraffin content than do heavy neutrals and that catalytic dewaxing removes more of the normal paraffins than does solvent dewaxing. Additional comparisons of solvent and catalytically dewaxed oils are provided in the section on catalytic dewaxing, see Chapter 8.

Table 2.21 Comparison of Solvent and Catalytically (ZSM-5) Dewaxed Oils

	Light neutral			Heavy neutral		
Composition	Feed	Solv.	ZSM-5	Feed	Solv.	ZSM-5
Paraffins	37.0	25.2	21.0	23	18	14
n-paraffins	15.0	0.9	0.2	2.5	—	—
Mononaphthenes	15.3	14.3	16.5	15	15	17
Polynaphthenes	24.9	34.0	34.7	24	24	27
Aromatics	23.0	26.4	27.9	38	43	43

Reprinted from Ref. [12] by courtesy of Mobil Research and Development Corp.

Table 2.22 Some Products Formulated from Naphthene Oils

Transformer oils	Cylinder lubricants
Refrigeration oils	Rubber process oils
Turbine oils	Process oils
Hydraulic oils	Greases

VII. FORMULATED LUBRICANTS

A listing of the types of lubricants formulated from mineral base oils is provided below.

Engine oils	Transmission fluids
Gear oils	Metal working fluids
Industrial oils	Hydraulic fluids
Greases	Speciality oils

A listing of some of the lubricants formulated from the different type base oils is provided in Tables 2.22 through 2.24.

VIII. SPECIALITY OILS

Table 2.25 provides a listing of speciality oils which are manufactured from both naphthenic and paraffinic feedstocks. These oils usually require more severe or more processing than conventional naphthene pale oils or solvent neutral oils.

Specifications for these products are usually established by original equipment manufacturers, governmental bodies and industrial associations which vary from country to country or, in the case of agricultural spray oils, from state to state. The U.S. specifications for technical and medicinal white oils specified by the U.S. FDA [13,14] are presented in Tables 2.26 and 2.27.

Although these specifications are presented as examples, it should be noted that the purity of these grades of oil are controlled using similar or other specifications in other countries.

Table 2.23 Some Products Formulated from Solvent Neutral Oils

Motor oils	Transmission fluids	Journal lubricants
Gear oils	Paper machine oils	Metal working oils
Turbine oils	Hydraulic oils	Greases

Table 2.24 Some Products Formulated from Bright Stocks and Cylinder Oils

Lubricant	Base oils used
Motor oils	Bright stocks
Hydraulic oils	Bright stocks
Greases	Bright stocks and cylinder oils
Gear oils	Bright stocks and cylinder oils
Cylinder lubricants	Bright stocks and cylinder oils
Journal lubricants	Bright stocks and cylinder oils

Table 2.25 Some Speciality Oils

Agricultural spray oils	EDM fluids
Transformer oils	White oils
Refrigeration oils	

Table 2.26 U.S. Technical White Oil Specifications

Specification	United States
Saybolt color	>20
Ultraviolet absorption of DMSO extract ASTM D 2269	
280-289 NM	4.0 Max
290-299 NM	3.3 Max
200-329 NM	2.3 Max
330-350 NM	0.8 Max

Prepared from Refs. [13] and [14].

Table 2.27 U.S. Medicinal Grade White Oil Specifications

Property	Specifications for Light mineral oil	Mineral oil
Density, 25°C	0.818–0.880	0.845–0.870
Viscosity, cSt @ 40°C	33.5 Max	34.5 Min
Saybolt color	Colorless	Colorless
Carbonizable substances	Pass	Pass
Neutrality	Pass	Pass
Paraffin content	Pass	Pass
Ultralviolet absorbance of UV absorbance of DMSO Extract at 260–420 NM	0.11 Max	0.11 Max

Prepared from Refs. [13] and [14].

IX. WAXES [15,16,17]

Wax generally refers to a substance which is a plastic-like solid at ambient temperature and which when heated becomes a liquid. Because wax is plastic it usually deforms under pressure without the application of heat. The chemical composition of waxes is complex and usually consists of a broad range of chemical species and reactive functional groups. Some different types of waxes are listed in Table 2.28 [16, 17]. Considerable information on these waxes are contained in the references. Since this section is concerned with petroleum waxes this discussion will be limited to the source, manufacture and composition of petroleum waxes.

A. Petroleum Wax

The quantity and quality of waxes manufactured from crude oils depends on the crude source and the refining to which it has been subjected. Some crude distillates are high in wax content while others contain very little wax. Some Sumatran, Russian, Chinese and some U.S. midcontinent crudes contain as much as 60 percent wax; the more typical lube distillates contain from 15 to 20 weight percent wax.

The separation of wax from a crude oil occurs during distillation. The distillate and DA oils are processed to remove asphalt, waxes, and aromatics, as was shown in Figure 1.1 of Chapter 1. Slack waxes from lube processing or very high wax content distillates are then deoiled and decolorized via clay treating or hydrogenation.

Petroleum wax consists of the hydrocarbon waxes listed below.

Paraffin wax. Substantial portion of normal paraffins.
Microcrystalline wax. Substantial portion of naphthene waxes.
Semimicrocrystalline wax. Mostly naphthene and aromatic waxes.

The paraffin waxes are usually derived from light (low viscosity) distillates, the semimicrocrystalline waxes are derived from the medium viscosity distillates with distillation end point above about 1000°F and the microcrystalline waxes are derived from high viscosity distillates and residual oils. The waxes obtained from residual oils are most often called petrolatums. Paraffin waxes are also called macrocrystalline waxes and semimicrocrystalline and microcrystalline waxes are called malcrystalline waxes.

Table 2.28 Types of Waxes

Beeswax (insect wax)	Vegetable (carnauba) wax
Spermaceti (animal) wax	Mineral (petroleum) wax
Synthetic (polyethylene and Fisher-Tropsch) waxes	

Table 2.29 Composition of Waxes from Solvent Dewaxing

Composition	Light neutral	Heavy neutral	Petrolatum
Paraffins	77.6	23	26
n-paraffins	68.0	15	<2
Mononaphthenes	16.4	37	21
Polynaphthenes	2.8	25	10
Aromatics	3.2	15	43

Note: Petrolatum is the wax from bright stock manufacture. Reprinted from Ref. [12] by courtesy of Mobil Research and Development Corp.

Data [12] shown in Table 2.29 show that normal paraffin and total paraffin contents are highest in the light wax and lowest in the heavy wax (petrolatum). Naphthenic wax content is higher in the heavy neutral wax than in either the light neutral wax or the petrolatum.

B. Wax Type and Properties

A listing of some tests used to set wax specifications is presented in Table 2.30. The specific tests used and limits are usually established by the customer. Some typical physical properties for petroleum waxes are shown in Table 2.31 [16].

C. Specifications for Petroleum Wax

Each country has adopted its own code governing materials which come into contact with food. These regulations usually address two concerns, 1) the wax

Table 2.30 Tests for Measuring Wax Properties

Property	Test method
Melting point	ASTM D 87
Drop melting point	ASTM D 127
Congealing point	ASTM D 938
Oil content	ASTM D 721
Viscosity	ASTM D 445
Needle penetration	ASTM D 1321
Cone penetration	ASTM D 937
Density	ASTM D1418
Refractive index	ASTM D 1747
Cleveland flash point	ASTM D 92
Saybolt color	ASTM D 156
ASTM color	ASTM D 1500

Table 2.31 Properties of Petroleum Wax

Property/Type of Wax	Paraffin	Microcrystalline
Flash point, °C(F)	204 (400) Min	260 (500) Min
Viscosity at 210°F, cSt(SUS)	4.2-7.4(40-50)	10.2-25(60-120)
Melting point, °C(F)	46-68(115-122)	60-93(140-199)
Refractive index at 100°C	1.430-1.433	1.435-1.445
Average molecular weight	350-420	600-800
C Atoms per molecule	20-36	30-75
Penetration at 25-C 1/10 mm	15-22	20-50
Physical aspects	Crystalline Friable	Ductile plastic to Tough-brittle

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must be refined and 2) the wax must not impart an unacceptable odor, taste or change in the nature of the wax. The level of refining considered sufficient is determined differently in different countries. However, an absorptivity of ultraviolet light below certain limits after extraction with specified solvents is common. A listing of the more important U.S. FDA requirements for food grade and non-food grade waxes are presented in Table 2.32 [13,14]. Additional requirements for petrolatums are specified in the U.S. Pharmacopeia and the National Formulary [14].

D. Use of Petroleum Wax

Some uses for fully refined (0.5 max oil content) waxes, scale (1-3 wt % oil content) waxes and slack (5-50 wt % oil content) waxes are summarized in Table 2.33 [15,16,17,18,19].

Table 2.32 U.S. FDA Requirements for Waxes and Petrolatums

	Petroleum wax	Petrolatum
Specific gravity, @ 60°C		0.818-0.880
Melting range, °C		38-60
Consistency, mm/10		100-300
Ultraviolet absorbance		
280-289 millimicron	0.15 maximum	0.25 maximum
290-299 millimicron	0.12 maximum	0.20 maximum
300-359 millimicron	0.08 maximum	0.14 maximum
360-400 millimicron	0.02 maximum	0.04 maximum

Prepared from Ref. [13] and [14].

Table 2.33 Some Uses for Wax

Petrochemical feedstocks	Candle manufacture
Hardboard manufacture	Carton manufacture
Paper coatings	Match inpregnation
Cosmetics	Textile softeners
Pharmaceuticals	Mold release agents
Lubricants	Metal protectors
Cosmetics	Chewing gum base
Crayons	Food coatings
Polishes	Casting waxes

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3

Lubricant Base Oil Distillation

I. INTRODUCTION

The crude distillation units are the major processing units in a petroleum refinery. They are used to separate the crude oil into the desired fractions according to their boiling point for use as products, blending stocks or as feedstocks to other processing units. These units consist of at least two sections, an atmospheric distillation unit (ADU) and a vacuum distillation unit (VDU). The ADU operates at essentially atmospheric pressure and the VDU operates under vacuum to remove the high boiling fractions. The ADU is usually used to prepare fuel fractions and petrochemical feedstocks. It is sometimes used to prepare some low boiling lube feedstocks such as EDM fluids, transformer oil or spindle oils. The VDU is used to prepare vacuum gas oils, lube feedstocks, vacuum residua and asphalts.

II. CRUDE DESALTING [1,2,3]

Inorganic salts, primarily sodium chloride, are found in the crude in a concentration of 5–100 g/bbl (10–200 lbs/1000 bbls); bottoms sediment and water (BS&W) is usually at a concentration of less than 1.5%. These impurities must be removed from the crude because they will form deposits in heat exchangers and heater surfaces causing high pressure drops which result in high fuel costs, high pumping costs, and short equipment life. The salts also hydrolyze to

hydrogen chloride in the heaters and dissolve in the water in the overhead condenser, forming a strong acidic solution which is corrosive.

A flow diagram for a desalting unit is shown in Figure 3.1 [2]. The raw crude oil is pumped to the desalting unit, exchanges heat with desalted crude leaving the unit, then picks up additional heat from steam (exhaust or live). Hot water is then injected at from 3 to 10 volume percent of the crude rate (6 bbls. water/100 bbls. crude oil) to aid in dissolving the salts. The water–oil mixture passes through a mixing valve and enters a settler where the oil and water phases are separated. Chemicals are sometimes used to assist with the separation and a high electrical potential of 16,000 to 35,000 volts is sometimes used to promote coalescence. Single stage units provide water separation efficiencies of 65 to 95 percent whereas two stage units provide efficiencies of 99 percent [1,3].

III. DISTILLATION [1,3,4,5,6,7]

After the water, salts, and sediment have been removed by desalting, the crude oil is separated into a series of narrow boiling fractions in a crude distillation unit (CDU), generally referred to as a vacuum pipe still (VPS). Simplified flow diagrams for a crude distillation unit are shown in Figures 3.2 and 3.3 [8,5]. These units consist of two distillation sections generally referred to as the atmospheric distillation tower or unit (ADT or ADU) and one or more vacuum distillation towers or units (VDT or VDU). The use of two VDUs operated in series is required to provide narrower and sharper lube fractions than are obtained using one VDU [5]. The better fractions obtained in this manner are reported to reduce processing severity and improve efficiency of downstream refining, dewaxing and finishing units which result in higher yields and longer catalyst life [5,9].

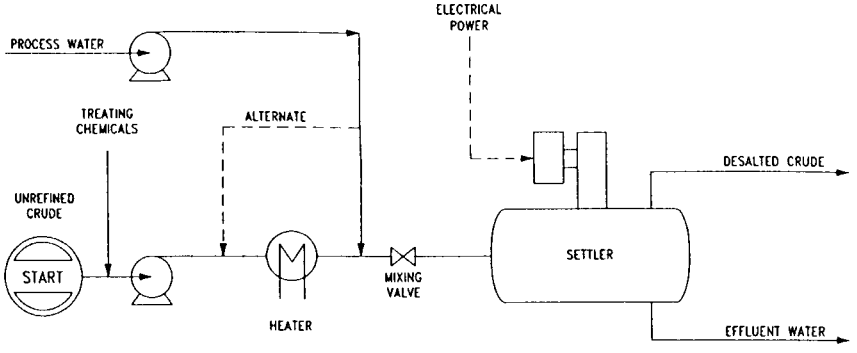

Figure 3.1 Crude desalting unit. (Reprinted by permission from *Hydrocarbon Processing*, Sept., 1990, Gulf Publishing Co.)

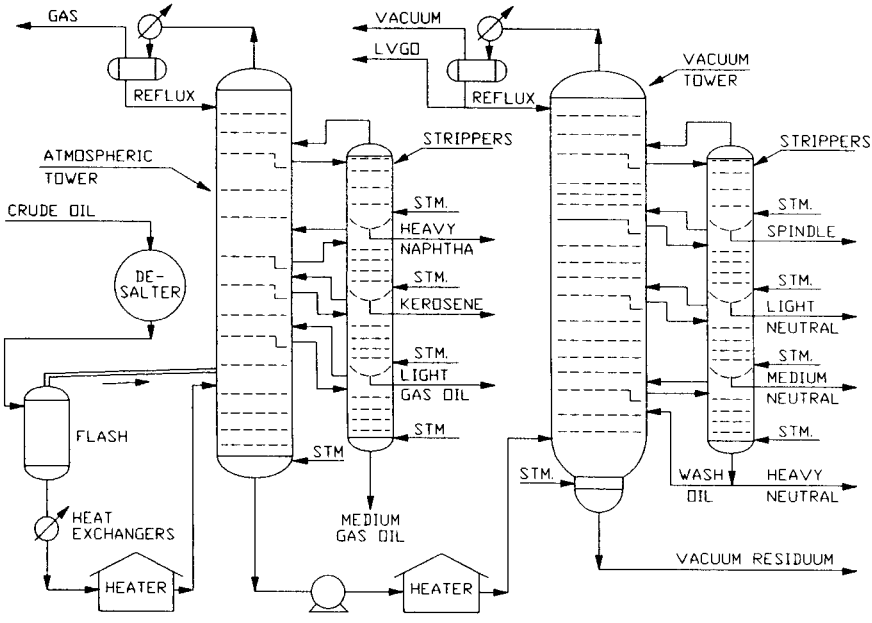

Figure 3.2 Two stage crude distillation unit. (Reprinted from Ref. 8, p. 352.)

A. Atmospheric Distillation

A description of the ADU operation is provided below with additional comments provided in Table 3.1.

The desalted crude oil is heat-exchanged and passed through a fired heater and heated under pressure (100–200 psig) to a temperature that will vaporize the materials to be removed at points above the flash zone of the ADU; the temperature will be a little higher than the heaviest material to be removed to ensure that some higher boiling material is vaporized. This higher temperature is used to provide better fractionation on the plates above the flash zone. The vapors leaving the flash zone are partially condensed as they travel up the ADU and the condensed vapors (liquid) create a reflux which improves the degree of separation. A portion of the condensed vapors from the overhead condenser is returned to the top of the ADU to provide the reflux for the fractionating tower.

B. Distillation Products

Table 3.2 presents the typical crude fraction cut points for distillation of crude oils in typical refineries.

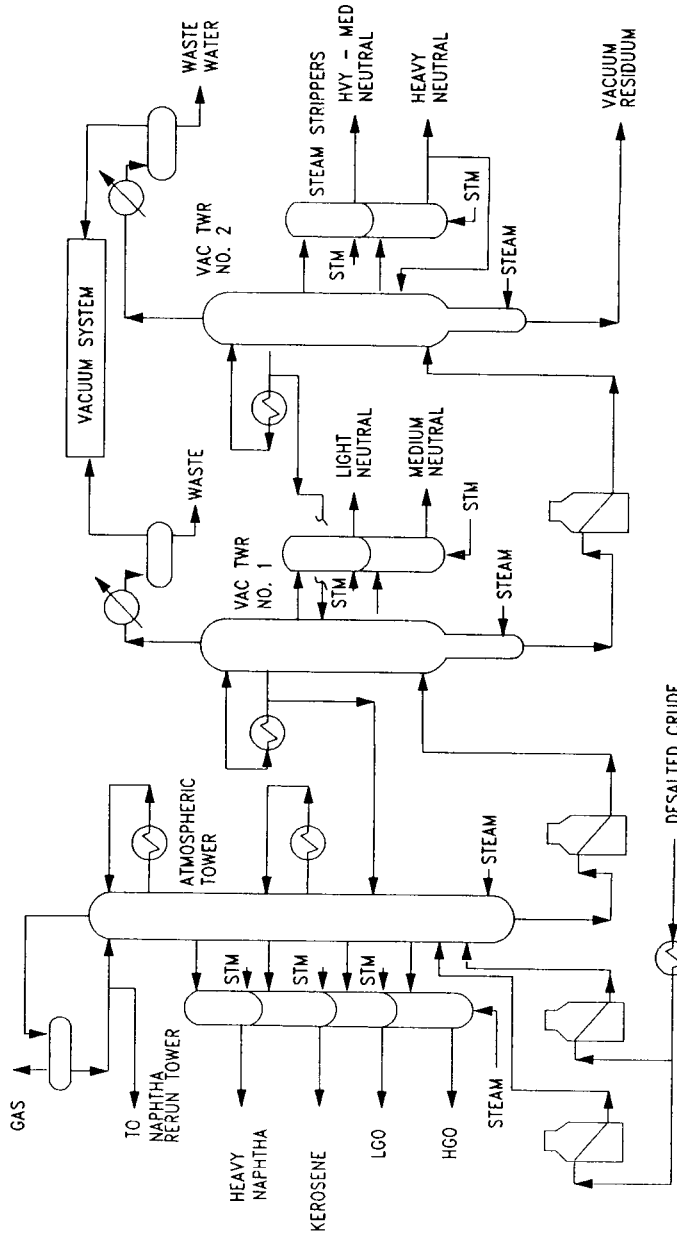

Figure 3.3 Three stage crude distillation unit. (Reprinted from Ref. 5, pp. 102–103 by courtesy of Foster Wheeler Corporation.)

Table 3.1 Operation of the Atmospheric Distillation Unit

Heat for fractionation
Provided by heat exchange, fired heater and steam
No reboiler is used
Reflux streams are vaporized
Fractionated products are removed by side strippers
ADU is controlled by heat and material balances
Temperature and draw rates determine boiling range
ADU top is temperature controlled by reflux and side draws
Steam is used to strip oil from the ADU flash zone
Pressure drop across ADU
Low pressure drop permits use of lower temperatures
Low pressure drop provides high yield of distillate.
Pressure drop depends on ADU internals and throughput
ADU internals
Trayed towers, packing

The boiling range of light base oils such as 40–60 neutrals, EDM fluids, transformer oils, etc., dictate that they be distilled on the ADU; they have cut point boiling ranges lower than those shown in Table 3.2. It should be noted that the boiling range of lube oil fractions is much narrower than that of vacuum gas oils used as FCCU feed. It should also be noted that the boiling

Table 3.2 Crude Fractions TBP Cutpoints

Atmospheric fractions		TBP cut point, °F
Gas and light ends		C1–C4
Light (LSR) naphtha		50–200
Heavy (HSR) naphtha		200–375
Kerosine		375–450
Diesel, heating oil		450–550
Atmospheric gas oil		550–650
Atmospheric residuum		650+
Vacuum fractions	**Fuels**	**Lubes**
Light lube distillate	—	625–725
Light vacuum gas oil	650–750	—
Medium lube distillate	—	725–825
Heavy vacuum gas oil	750–1000	—
Heavy lube distillate	—	825–1050
Vacuum residuum	1000+	1050+

range of the lube fractions is much wider than the cut point ranges presented in Table 3.2. A comparison of the lube fraction boiling ranges with the cut points on the reduced crude is shown in Figure 3.4. The data in Figure 3.4 show that the lube fraction boiling ranges are about 250 to 400°F in comparison to crude cut points of 100 to 150°F. The data also show that there is considerable overlap in the boiling range of the lube fractions.

C. Vacuum Distillation

The atmospheric residuum or reduced crude leaving the bottom of the ADU passes through a fired heater into the flash zone of the VDU where it is fractionated into lube distillates. Steam is introduced into the VDU flash zone to lower the vapor pressure of the distillates and permit removal of high boiling hydrocarbons. Additional comments concerning VDUs are provided in Table 3.3.

Table 3.4 provides information and general comments on the internals used in crude distillation units.

The design and operation of the VDU is of utmost importance in the manufacture of lube base stocks because distillate properties, particularly boiling range and purity of the feedstocks have a significant effect on processing response in the lube refining, dewaxing and finishing units as well as the quality and yield of the finished base stock. It is for these reasons that lube VDUs

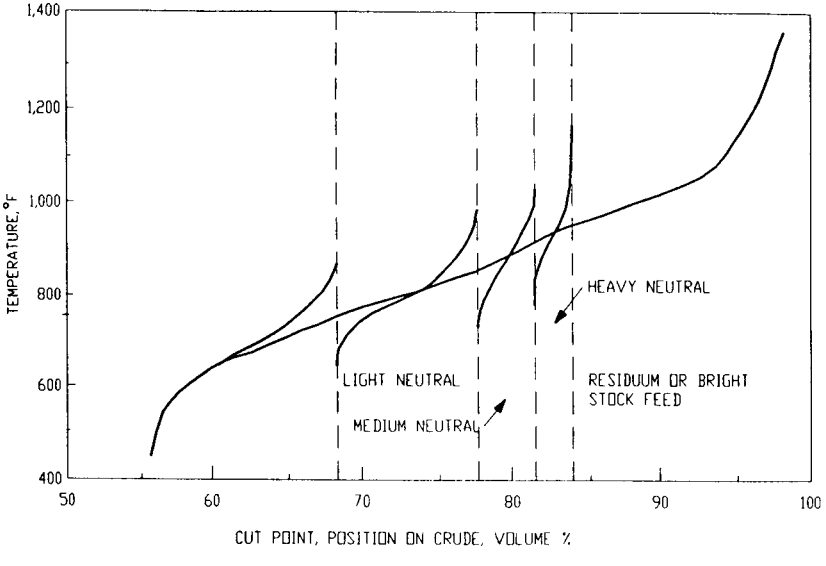

Figure 3.4 Comparison of boiling ranges for distillates and atmospheric residuum.

Table 3.3 Operation of the Vacuum Distillation Unit

Feedstocks
Atmospheric residua
Vacuum gas oils (vacuum rerun units)
Products
Vacuum gas oils and vacuum residua for further processing
Lube distillates removed through side strippers
Heat for fractionation
Provided by heat exchange, fired heaters and steam
No reboiler is used; the reflux streams are vaporized
VDU controlled by heat and material balances
Temperature, vacuum and draw rates determine boiling range
Top temperature is controlled by reflux and side draws
Pressure and temperature
Maximum temperature 650–750 °F
Pressure range 20–100 mm Hg with steam
Pressure range 10–40 mm Hg without steam
General comments
Pressure drop is critical
Low pressure drop provides high distillate yield
Large diameter towers reduce pressure drop
Packing provides low pressure drop
Feed rates are lower than ADU feed rates

contain more fractionation stages, operate at lower vacuum and use more reflux than VDUs used to prepare vacuum gas oils for fuels manufacture [4].

Figure 3.5 presents the boiling range distribution for some 325 neutral distillates of essentially the same viscosity and flash point produced from the same crude oil using four different vacuum distillation units. These data show that each unit produced distillates of different boiling ranges. These differences result from differences in design and operation of the vacuum distillation units.

Refiners have in recent years refurbished existing VDUs and/or installed new VDUs with high efficiency internals to reduce the flash zone pressure and improve the purity and yield of lube oil distillates obtained from lube crudes [6,10,11,12,13]. These changes result in improved processing response in downstream units and improve base oil volatility. Figure 3.6 presents boiling range data for a 325 neutral distillate produced on the same vacuum distillation unit before and after the internals of the vacuum distillation unit were modified. These data show that the distillate had a narrower boiling range after the modification. In addition, the capacity of the refining and dewaxing units were improved after the vacuum distillation unit was revamped.

Table 3.4 Crude Distillation Unit Internals

Pressure drop
High liquid hold up: 8–12 %
8–12 % for trays
1–6 % for sieves
Bubble cap trays
Higher pressure drop
Low vapor capacity
Generally not used
Sieve trays
Flat plate with holes
High vapor capacity
Valve trays
Plate with valves
Capacity like sieve tray
Random packings
Ballast rings, pall rings
Flexirings, minirings
Saddles
Structured packing
Knitted or corrugated plates as beds
Higher efficiency than random packing
Higher cost than random packing
Structured grids
Rigid grids rotationally stacked in layers

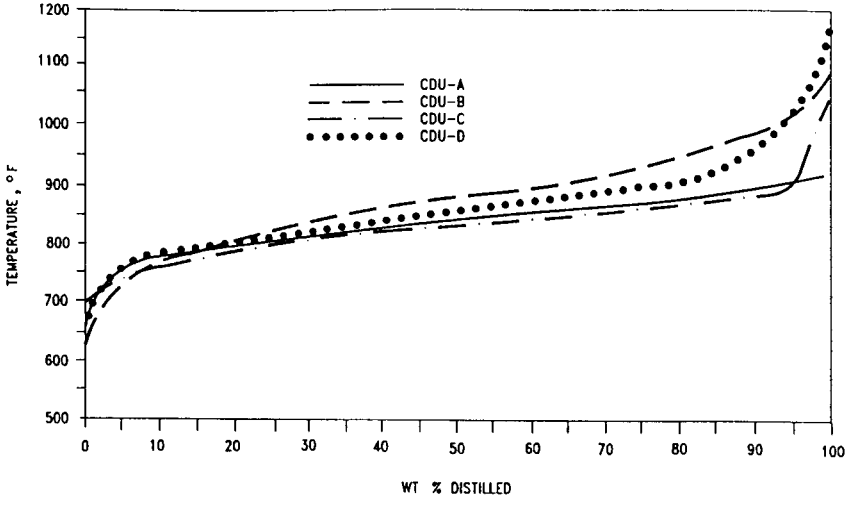

Figure 3.5 Boiling range of some 325 neutral distillates.

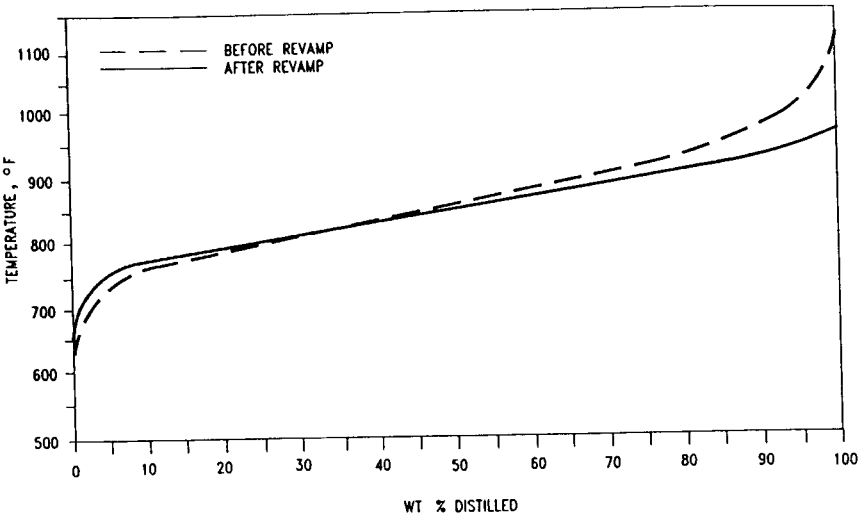

Figure 3.6 Effect of modifying VDU internals on distillation of 325 neutral.

The use of lower absolute pressure in the flash zone and use of the VDU wash oil reflux stream as feed to the deasphalting unit permits the manufacture of higher viscosity base oils at higher yield and permits the refiner to improve the economics of the deasphalting process. The reported benefits include 1) a 15 percent reduction in VDU feed, 2) a 30 percent reduction in lube distillates to the fuel pool and 3) a 10 percent reduction in lube by-products to fuels [13].

In some cases a solution of caustic or lime is introduced into the feed to the CDU or VDU for the purpose of neutralizing the organic acids present in the crude oil [7,14,15]. The purpose for neutralizing the acids in this manner is to remove organic acids and prevent corrosion in the crude stills and/or downstream processing units. Another advantage obtained from crude oil neutralization is an improvement in color, stability and refining response of the lube distillates [7].

IV. INVESTMENT AND UTILITY REQUIREMENTS

The investment and utility requirements for crude distillation units are site- and unit design-specific and are highly dependent on the crude being used as well as the products being produced. In addition, the investment and utility requirements for a crude distillation unit for the production of lubricating oil feedstocks will be greater than that for a unit used to produce feedstocks for fuels processing units. It is, therefore, recommended that costs and utilities be obtained by consulting refiners and engineering and construction firms with

experience in design and construction of these units using the crude to be processed.

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4

Lubricant Base Oil Deasphalting Processes

I. INTRODUCTION [1–6]

Most crude oils contain varying amounts of high molecular weight hydrocarbons (asphaltenes and resins) which are solid to semisolid in nature with high carbon to hydrogen ratios. The asphaltenes are nonvolatile and thus tend to remain in the residue on heating. The resins are in part volatile and may be present in some of the high boiling lube distillates. Since these fractions contain many high viscosity components useful in the manufacture of lubricating oils, refiners have employed many methods (adsorption, chemical treating and precipitation with alcohols, ketones and light hydrocarbons) to remove these asphaltic materials from heavy distillates and vacuum residuum. Propane deasphalting and the Duo-Sol process are most often used to remove these materials. The Duo-Sol process is a combination propane-deasphalting and solvent-refining process which uses Selecto (a mixture of phenol and cresylic acids) as the extraction solvent. The asphalt and resins present in the very heavy distillates and residua are removed because they are high in viscosity, seriously impede the refining action of other processes, contribute an undesirable dark color to lube base stocks and have a tendency to form carbonaceous material and deposits on heating.

Propane deasphalting (or propane deresining when used to remove resins from Pennsylvania grade vacuum residua) is an extractive-precipitation process which selectively precipitates asphalt, resins and hydrocarbons on the basis of

Table 4.1 Effects of Lube Deasphalting on Physical Properties

Decreases asphaltene content	Decreases aromatic content
Decreases resin content	Decreases nitrogen content
Decreases carbon residue	Decreases sulfur content
Decreases metals content	Decreases viscosity
Increases pour point	Feedstock dependent
Increases API gravity	Increases wax content
Improves color	Increases hydrogen content

density and the invert solubility of the heavy hydrocarbons in liquefied light hydrocarbons. Propane is preferred over the other liquefied gases used in the milder "deep" deasphalting (sometimes called decarbonizing) processes to prepare feedstocks for fuels processing, because considerably more asphalt and resins must be precipitated to prepare a deasphalted oil (DAO) which can be used for the manufacture of lube base stocks.

Deasphalting is an extractive-precipitation process. The purpose of the process is the removal of asphaltenes, resins and metals from vacuum residua and very heavy vacuum gas oils. Propane can also be used to fractionate distillates and other hydrocarbons on the basis of density. When used in this manner it is called propane fractionation. The effects of deasphalting on properties of the lube feedstock are summarized in Table 4.1. Although the process is primarily used to remove asphaltic materials from the feedstock, it also removes other undesirable materials such as sulfur, nitrogen, aromatics and metals. It also improves the color and viscosity index of the feedstock. Accompanying these beneficial changes one accepts the increase in wax content of the deasphalted oil. The feedstocks to deasphalting and the products from deasphalting are listed in Table 4.2.

The deasphalted oils from atmospheric residua and very heavy vacuum distillates are used as feedstocks to lube processing units for the manufacture of lube base oils ranging from solvent neutral oils to cylinder oils and bright stocks. Deasphalted oils from the deep deasphalting processes are used as feedstocks to cat cracking or hydrocracking units. The residue, asphaltenes and

Table 4.2 Feedstocks and Products

Feedstocks	Products
Vacuum residua	Deasphalted oils
Atmospheric residua	Asphaltenes
Heavy vacuum gas oils	Resins

Table 4.3 Deasphalting Process Variables

Solvent	Feedstock
Solvent composition	Temperature
Solvent-to-feed ratio	Pressure

resins from deasphalting are used as asphalt extenders, coker feed, or as a component of fuel oil.

II. DEASPHALTING PROCESS VARIABLES [1,2,5]

The major process variables are listed in Table 4.3. The more important variables are the quality of the feedstock, the solvent and the deasphalting temperature.

The process conditions used in lube deasphalting are summarized in Table 4.4. The temperature and dosage are the process conditions which are most often varied with the quality of the feedstock and the DA oil quality being the major determinants of these process conditions. Although solvent dosage as high as 15 or more may be used to maximize DA oil yield, the dosage used will depend on the quality of the feedstock and product being manufactured. The more typical range for solvent dosage is probably about 800–1000 volume percent propane to residua for the manufacture of bright stocks.

A. Feedstock

The effect of feedstock on yield and DA oil properties for preparation of lube feedstocks is shown in Table 4.5 [1]. These data show that crude source and length of the residuum are important process variables. Heavy neutral distillates are also sometimes produced by deasphalting the wash oil stream from vacuum fractionation of reduced crudes [1]. The yield of DA oil for use in bright stock and cylinder oil manufacture can be increased by the inclusion of a higher than normal proportion of wash oil in the vacuum residuum used as feed to the deasphalting unit [7]. In addition to the reported benefit of lower investment cost, use of this technique results in a higher yield of DAO and a lower

Table 4.4 Propane Deasphalting Conditions

Solvent dosage, vol %	500–1500
Temperature, °F	100–190
Pressure, psig	350–550
Deasphalted oil yield, vol %	30–90

Table 4.5 Yields and Product Properties for Deasphalting of Base Oil Feedstocks

Crude source	Oklahoma	Peru	East Texas	Kuwait	Kuwait
Vacuum residuum					
API gravity	19.3	14.9	14.3	8.6	5.4
SUS viscosity @ 210°F	385	740	920	950	23,000
Con carbon, wt %	7.3	6.7	11.5	16.0	24.0
Deasphalted oil					
Yield, vol % on feed	77.0	76.3	60.0	36.8	25.0
API gravity	23.3	19.4	23.0	24.3	21.2
SUS viscosity @ 210°F	150	207	155	94	163
Con carbon, wt %	1.7	1.7	1.5	0.7	1.3

Reprinted from Ref. [1], p. 153.

operating cost per barrel of feed and product for both new and existing propane deasphalting units.

The data presented in Table 4.6 are for the preparation of FCCU feed by deasphalting [1]. A comparison of the data in Tables 4.5 and 4.6 shows that the carbon residue and yield for deep deasphalting is higher than for lube manufacture; the high carbon residue FCCU feeds would not be suitable for quality base oil manufacture.

B. Solvent-to-Oil Ratio and Temperature

The general effects of solvent-to-oil ratio and temperature on the yield and quality of the deasphalted oil from virgin residua are presented in Table 4.7 and in Figures 4.1 through 4.4.

Table 4.6 Yields and Product Properties for Deasphalting for FCCU Feedstocks

Crude source	West Texas	Arab	Calif	Canada	Kuwait	Kuw
Vacuum residuum						
API gravity	12.0	6.8	6.3	9.6	5.6	8
SUS viscosity @ 210°F	526	75,000	9,600	1,740	14,200	3,270
Con carbon, wt %	12.1	15	22.2	18.9	24.0	19
Deasphalted oil						
Yield vol % on feed	66.0	49.8	52.8	67.8	45.6	54
API gravity	19.6	18.1	18.3	17.8	16.2	17
SUS viscosity @ 210°F	113	615	251	250	490	656
Con carbon, wt %	2.2	5.9	5.3	5.4	4.5	5

Reprinted from Ref. [1], p. 153.

Table 4.7 Effects of Deasphalting Solvent-to-Feed Ratio and Temperature

At constant temperature, increasing solvent-to-feed ratio:
Increases DA oil yield, viscosity and carbon residue
Increases DA oil metals, sulfur and nitrogen content
Decreases DA oil API gravity and viscosity index
At constant solvent-to-feed ratio, increasing temperature:
Decreases DA oil yield, viscosity and carbon residue
Decreases DA oil metals, sulfur and nitrogen content
Increases DA oil API gravity and viscosity index
At constant yield, increasing temperature and solvent dosage:
Increases DA oil API gravity and viscosity index
Decreases viscosity and carbon residue
Decreases DA oil metals, sulfur and nitrogen content

Deasphalting solvents behave like extraction solvents when the solvent dosage is increased at constant temperature; the amount of hydrocarbon soluble in the solvent increases. However, the deasphalting solvents exhibit and invert solubility in comparison to extraction solvents with an increase in temperature; the amount of hydrocarbon decreases with an increase in temperature. The deasphalting solvents also behave differently when both solvent and temperature is increased. In extraction, the amount of hydrocarbon soluble in the sol-

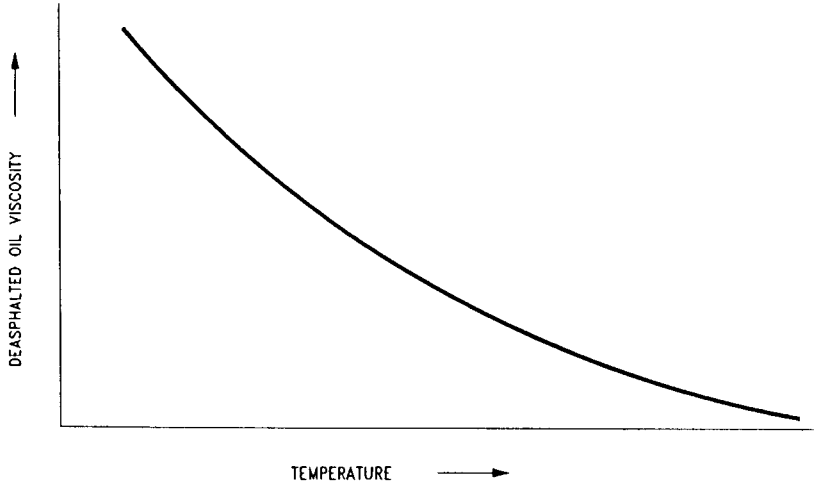

Figure 4.1 Propane deasphalting at constant dosage: effect of temperature on deasphalted oil viscosity.

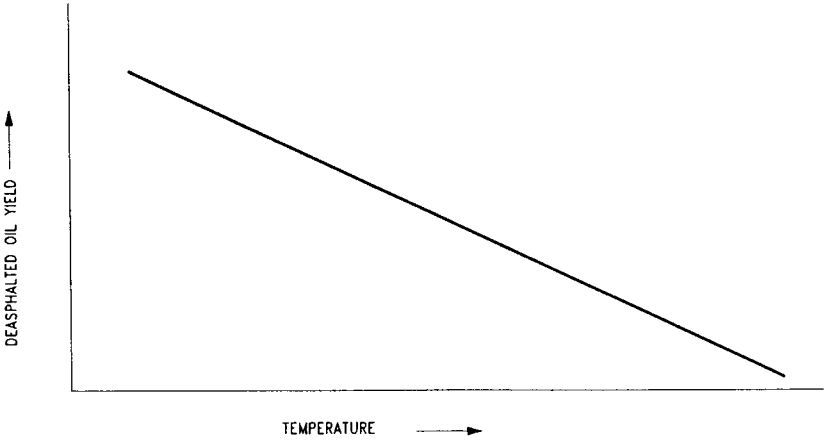

Figure 4.2 Propane deasphalting at constant dosage: effect of temperature on deasphalted oil yield.

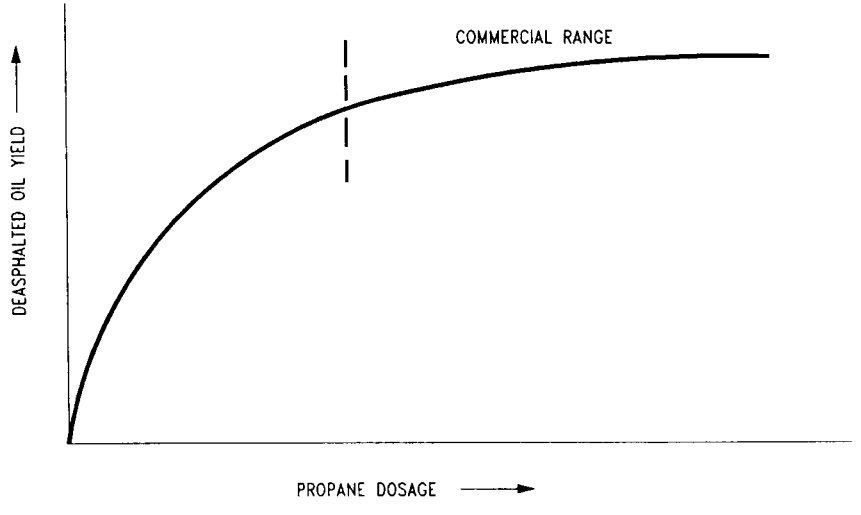

Figure 4.3 Propane deasphalting at constant temperature: effect of dosage on deasphalted oil yield.

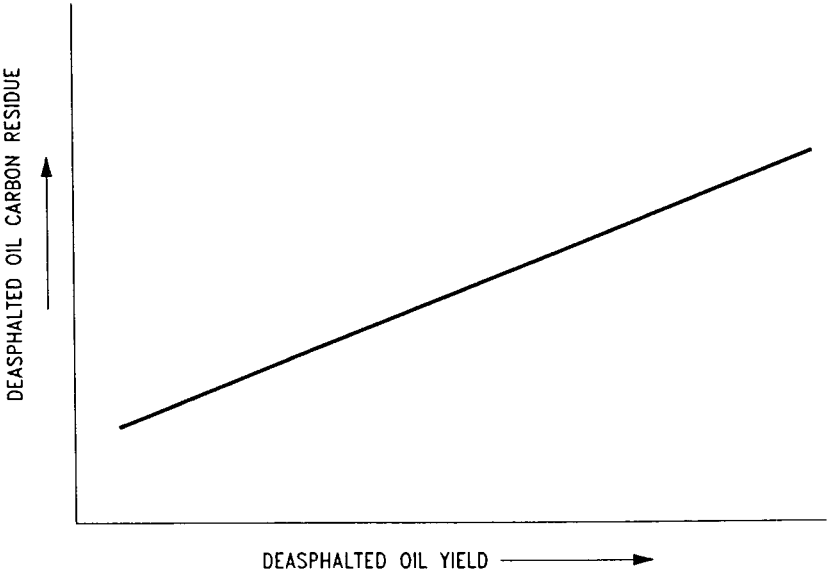

Figure 4.4 Propane deasphalting: carbon residue versus yield.

vent increases and with a deasphalting solvent the solubility may increase or decrease depending on the increase in either solvent dosage or temperature.

An increase in solvent dosage, with the appropriate increase in temperature, will almost always improve the quality of the DA oil at a given yield. However, this may not be cost-effective when one considers that the investment and operating costs of the deasphalting unit are proportional to the solvent dosage. It is therefore apparent that selecting an optimum solvent-to-oil ratio depends on the solvent and temperature used to prepare the desired DA oil from a given feedstock. Other factors which influence the processing conditions are the site, investment and operating costs.

The information available concerning the effect of solvent-to-oil ratio indicates that the optimum solvent dosage depends on the quality of the feedstock. Zuiderweg [8] presents data which shows that the quality of the deasphalted oil continues to improve with an increase in solvent-to-oil ratios as high as 10 to 1, but that metals removal is only slightly influenced by solvent ratios above about 5 to 1. Johnson et al. [9] report that increasing the solvent-to-oil ratio to about 15:1 results in better quality cracking stocks.

Control of the deasphalting tower becomes very difficult near the critical point of the solvent because the solubility of hydrocarbons in the solvent with temperature becomes very large at the critical point. This change in solubility

results in drastic changes in the amount of oil transferred between the raffinate and extract phases which causes flooding and DA oils of variable quality [1].

Although no separations are currently being made in the supercritical region, solvent is being separated from the deasphalted oil using supercritical techniques [3,6,10,11,12].

Temperature gradients are used in the deasphalting devices because they create internal reflux and increase the sharpness of the separation in the bottom of the deasphalting tower [1,2]. Low temperatures may impede mass transfer leading to inefficient operation.

C. Pressure

An increase in temperature decreases the yield and carbon residue content of the deasphalted oil. An increase in pressure increases the density of the solvent and increases the yield and decreases the quality of the DA oil. The effect of pressure becomes more evident as operating conditions approach the critical point. Pressure is normally not used for operational control of the deasphalting tower because of the instability of the separation and quality of the DA oil near the critical point.

D. Solvent and Solvent Composition

The solubility of a vacuum residuum in various light hydrocarbons is depicted in Figure 4.5. It should be noted that Figure 4.5 depicts the general shape of

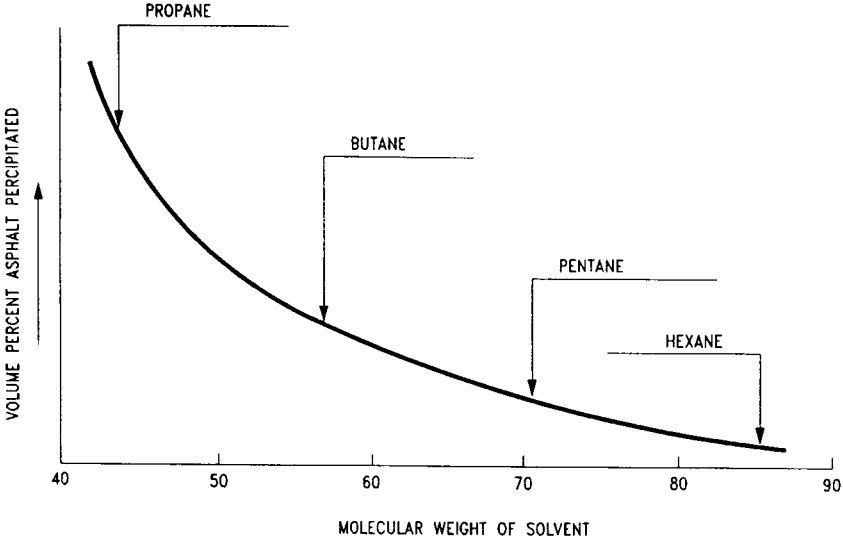

Figure 4.5 Selectivity of normal hydrocarbons.

the curve. The results obtained with different residua will be different at different temperatures and solvent-to-oil ratios. It is obvious from this curve that the solvent power of the deasphalting solvent can be controlled by selecting various mixtures of these solvents. This is done by some refiners. The lower molecular weight hydrocarbons have the lower solvent power and will precipitate more asphalt. It has generally been found that propane is more suited for the manufacture of lube feedstocks because greater quantities of the asphaltenes and resins must be removed to produce a quality base oil as compared to preparation of cracking feedstocks. Butanes and pentanes are generally used to prepare FCCU and hydrocracker feedstocks because they provide a higher yield of DA oil, and precipitate less of the asphalt than does propane.

The deasphalted oil quality relationships when using different deasphalting solvents as reported by Sprague [13] are presented as Figures 4.6 to 4.11. These deasphalting studies were conducted at a constant solvent-to-feed ratio of about eight while increasing temperature. The data show the effect of propane, butane and pentane on the deasphalted oil yield and quality of a mid-continent vacuum residuum. Similar data and behavior can be developed for other feedstocks; however, the shape and location of the curves will vary as a result of differences in the residuum composition.

III. PROCESS FLOW

Although mixer-settlers were used in the early deasphalting units, baffle towers of various designs and rotating disc contractors are used in modern deasphalting units. A simplified flow diagram for a unit using a mixer–settler is shown in Figure 4.12 [14].

A. Mixer–Settler Deasphalting Unit

In the older mixer–settler type of unit, the feedstock is combined with propane and mixed using a mixing valve or static mixer and flows to the asphalt settler. The solvent rich (extract) phase containing a partially deasphalted oil exits the top of the settler, is heated to a higher temperature and flows into the resin settler. The solvent rich extract phase containing the DA oil exits the top of the resin settler, is heated and flows to the solvent recovery section. Propane is separated from the DA oil using a high pressure and low pressure evaporator followed by steam stripping. The propane is condensed and/or compressed and flows to propane storage for reuse in the process. The raffinate, solvent-lean phase rich in asphaltenes, settles in the asphalt settler and the solvent-lean resin-rich phase settles in the resin settler. These phases flow from the bottom of the settlers and are mixed with propane before entering wash settlers. The propane-rich phase contains very small quantities of oil and flows from the

(*text continues on page 68.*)

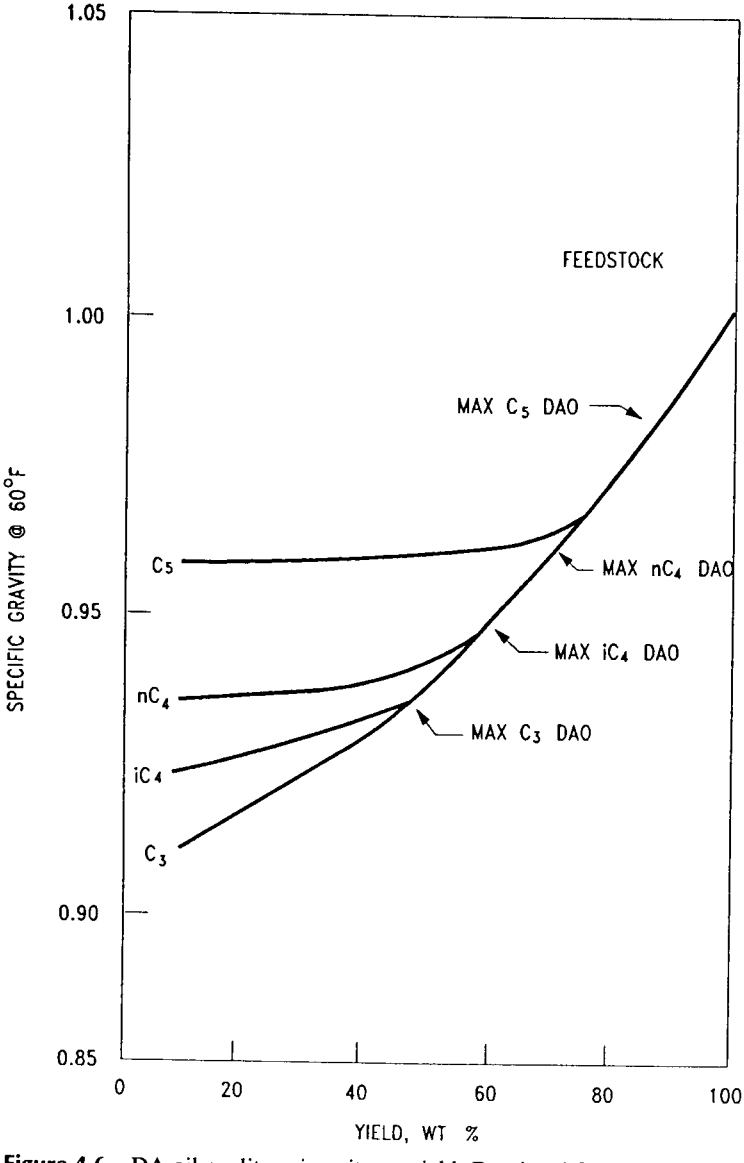

Figure 4.6 DA oil quality: viscosity vs yield. Reprinted from Ref. [13] by courtesy of Kerr-Mcgee Corporation.

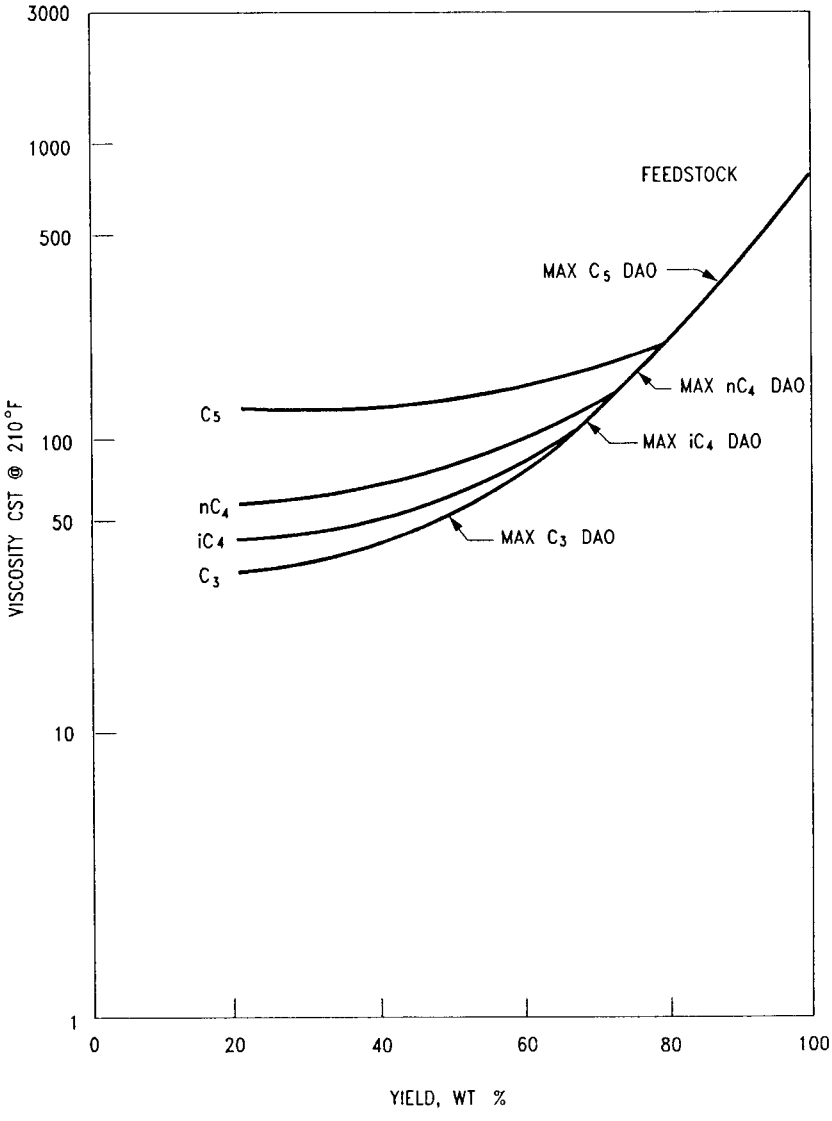

Figure 4.7 DA oil quality: specific gravity vs yield. Reprinted from Ref. [13] by courtesy of Kerr-Mcgee Corporation.

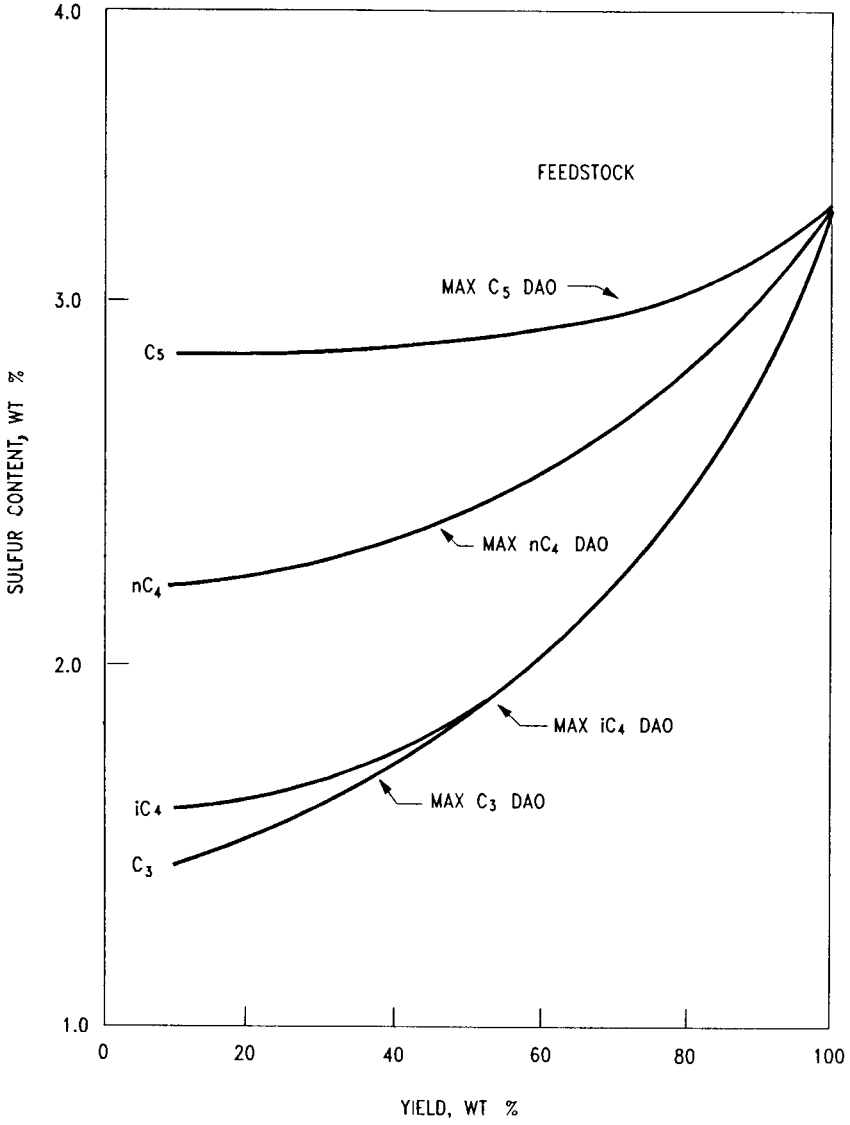

Figure 4.8 DA oil quality: sulfur content vs yield. Reprinted from Ref. [13] by courtesy of Kerr-Mcgee Corporation.

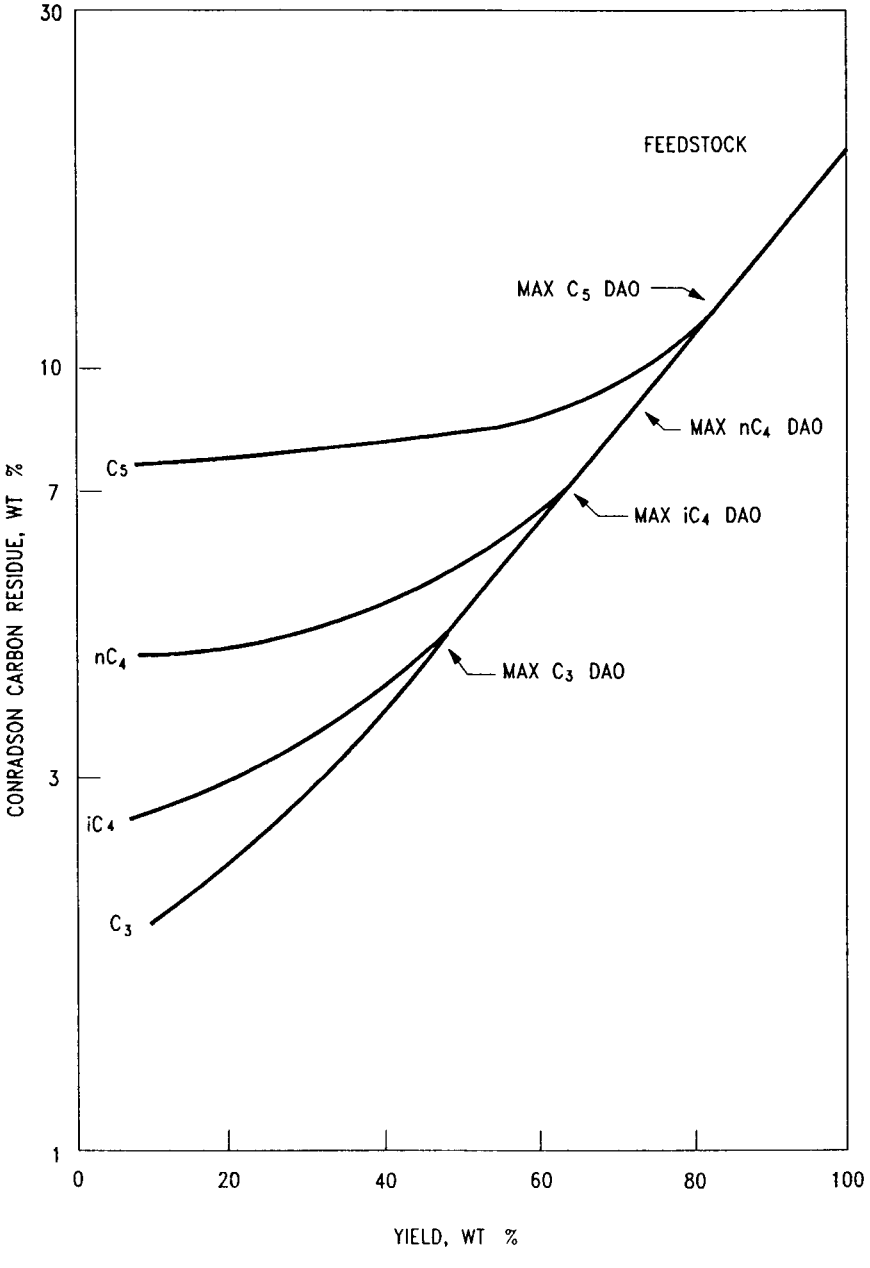

Figure 4.9 DA oil quality: conradson carbon vs yield. Reprinted from Ref. [13] by courtesy of Kerr-Mcgee Corporation.

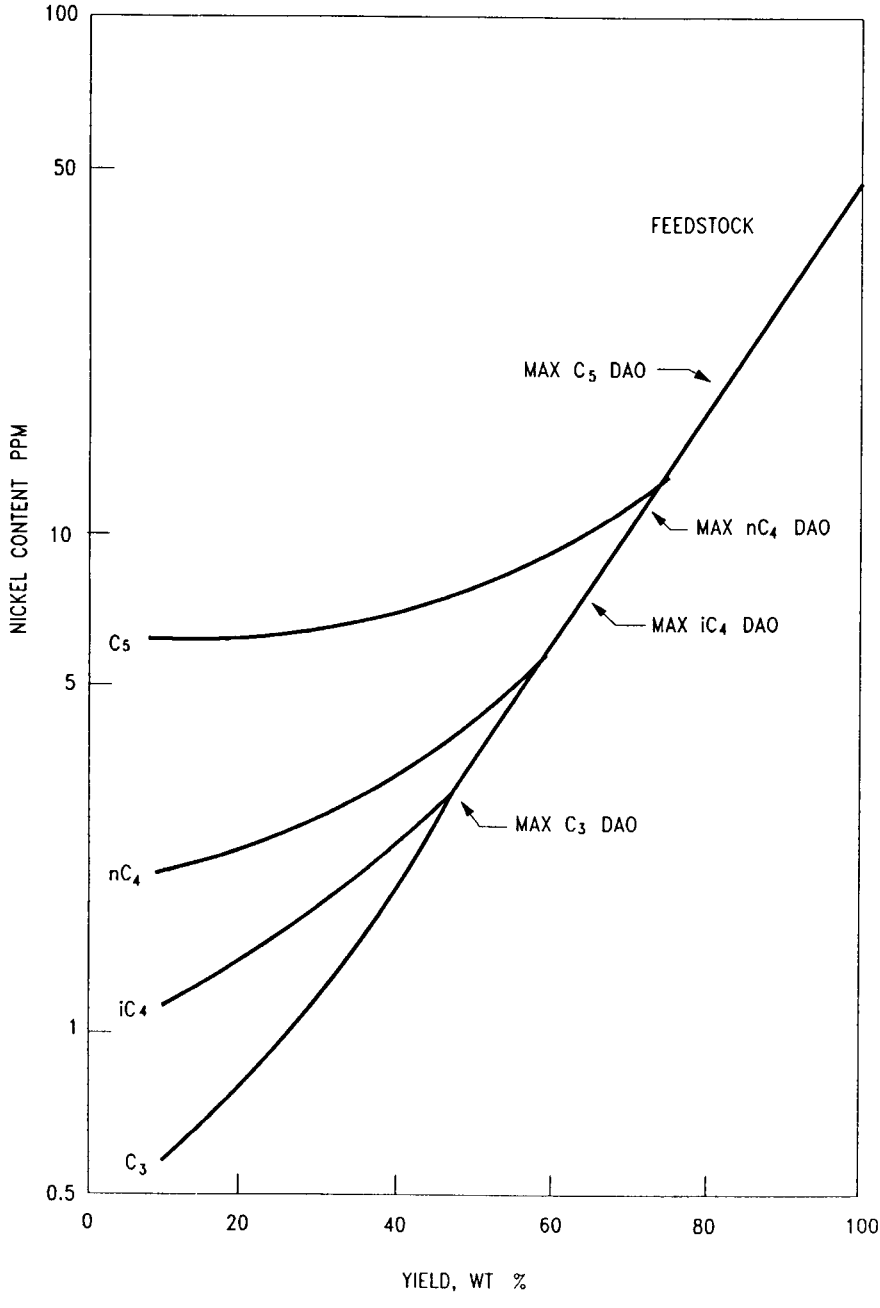

Figure 4.10 DA oil quality: nickel content vs yield. Reprinted from Ref. [13] by courtesy of Kerr-Mcgee Corporation.

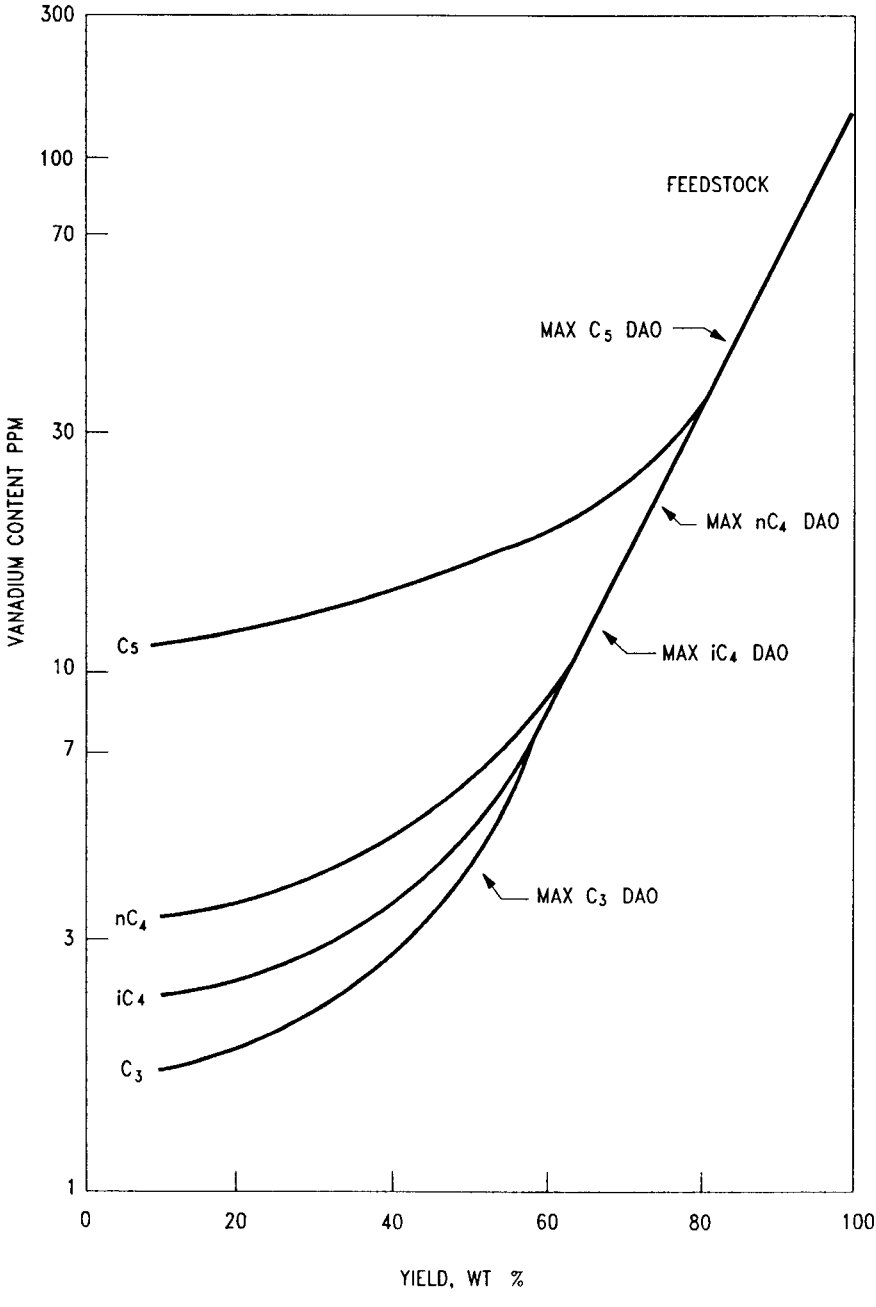

Figure 4.11 DA oil quality: vanadium content vs yield. Reprinted from Ref. [13] by courtesy of Kerr-Mcgee Corporation.

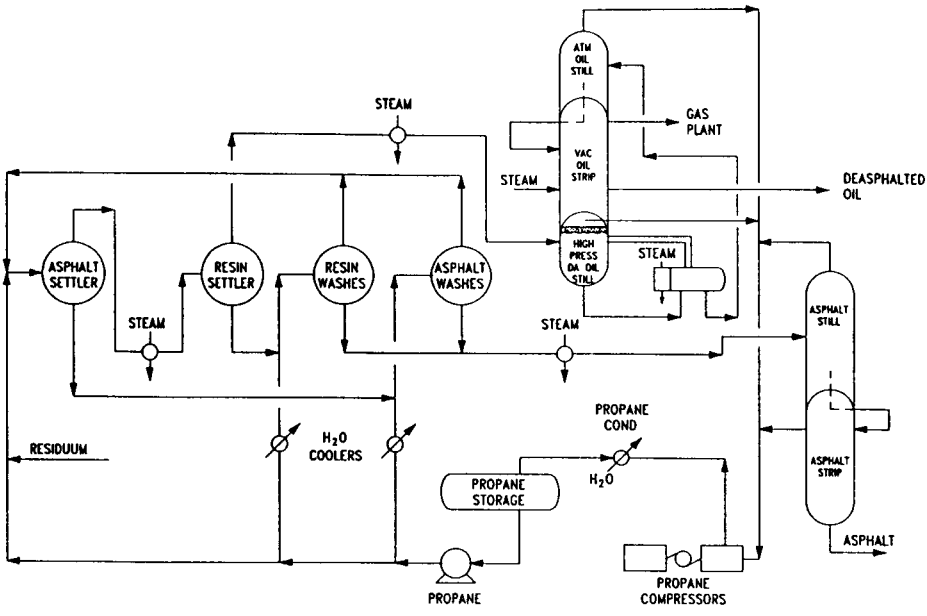

Figure 4.12 Mixer-settler deasphalting unit. Reprinted from Ref. [14] by courtesy of *Industrial and Engineering Chemistry*.

resin and asphalt wash settlers to combine with the feedstock entering the unit. The asphaltenes and resins are heated and recovered by flash distillation and steam stripping. The evaporated propane is condensed and/or compressed and flows to the propane storage tank for reuse in the process.

B. Continuous Deasphalting Units [2,3,4]

In modern deasphalting units the feedstock is combined with a small amount of propane to reduce viscosity. The prediluted feedstock is then pumped to a treating tower and enters at a point located in the upper part of the treating tower as depicted in Figure 4.13. The feed is countercurrently contacted therein with propane which enters near the bottom of the treating tower. The extract or solvent-rich phase consisting of a solution of deasphalted oil and propane leaves the top of the treating tower; the raffinate or solvent lean phase containing a solution of the residue or asphalt and propane leaves from the bottom of the treating tower. The solvent recovery techniques used will depend on the type of solvent recovery system being used and if resins are being separated from the asphaltenes.

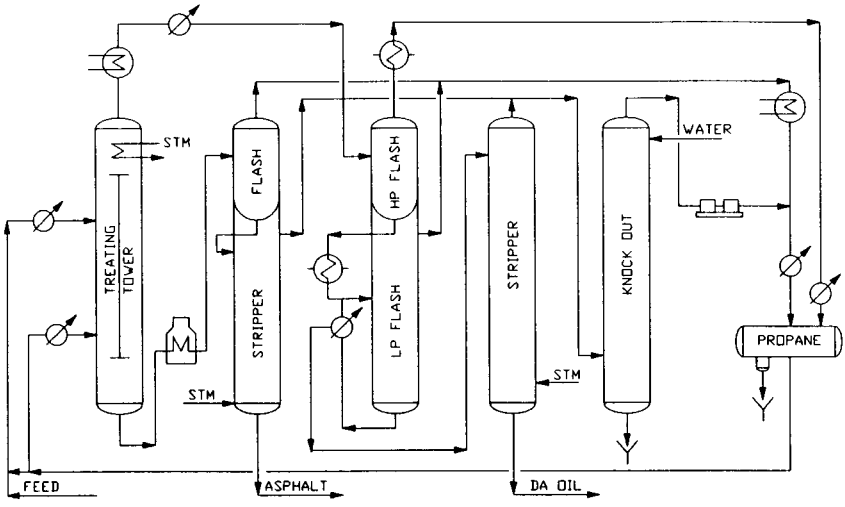

Figure 4.13 Propane deasphalting unit flow diagram. Reprinted from Ref. [15], p. 354.

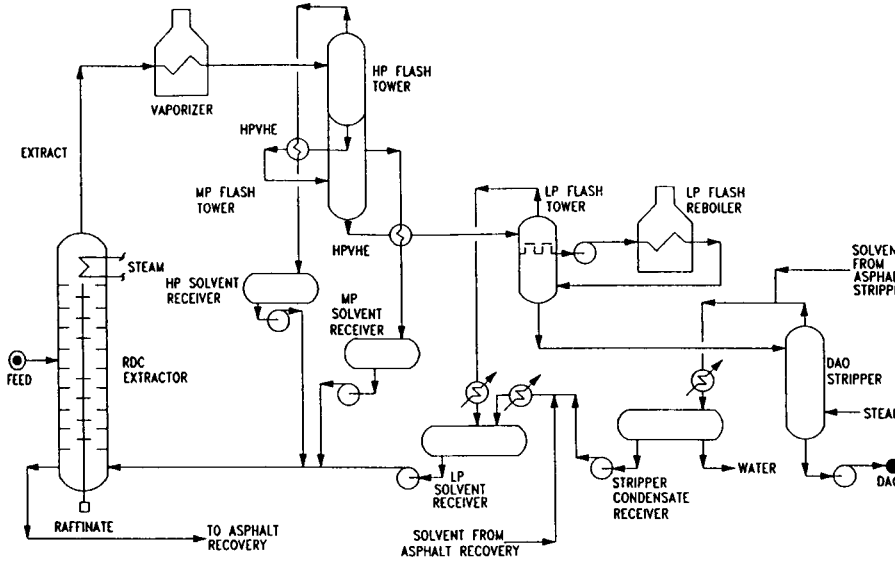

Figure 4.14 Deasphalting unit flow diagram: three stages of evaporation. Reprinted from Ref. [2] by courtesy of Foster Wheeler Corporation.

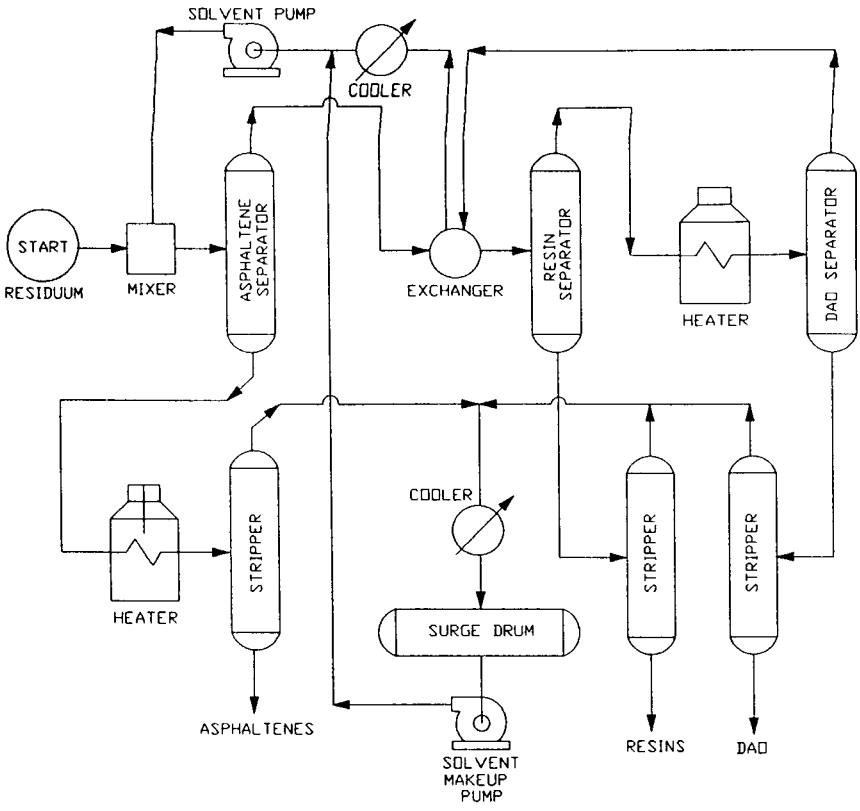

Figure 4.15 ROSE® Process flow diagram. Reprinted from Ref. [3] by courtesy of Kerr-McGee Corporation.

IV. SOLVENT RECOVERY TECHNIQUES

A summary of the solvent recovery techniques being used in deasphalting units is provided in Table 4.8. Although flash vaporization is the most widely used method, many new units use and several older units have or are being revamped to use the supercritical solvent recovery techniques.

A. Multiple Effect Evaporation

For units using multiple effect evaporation, the propane is recovered from the raffinate and extract phases using multistage flash vaporization and steam stripping. The water is removed from the propane by condensation and the propane is recirculated in the process as is done in the older mixer–settler units. The

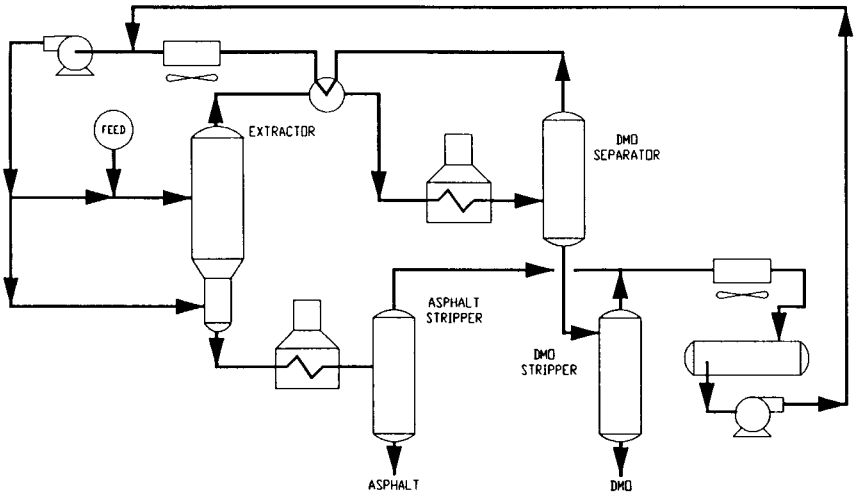

Figure 4.16 Supercritical Demex Unit flow diagram. Reprinted by courtesy of UOP.

effluent DA oil is cooled and sent to tankage for further processing. The residue from deasphalting is also sent to tankage for further processing or use in asphalt manufacture or fuel oil.

The main difference between the process flow of the units presented in Figures 4.13 and 4.14 is the number of evaporation stages used to recover the solvent from the deasphalted oil. The unit in Figure 4.13 uses two stages of evaporation as compared to three stages for the unit depicted in Figure 4.14. Units using three stages of evaporation use about two-thirds of the energy required for recovery of solvent from the DA oil mix in a two stage unit.

Single effect evaporation is used in some older deasphalting units with dual effect evaporation being used in most deasphalting units and triple effect evaporation being used in some modern and in some refurbished deasphalting units [2]. The two- and three-stage flash vaporization units use about 45 to 65

Table 4.8 Solvent Recovery Techniques

Conventional solvent recovery	Supercritical solvent recovery
Single effect evaporation	ROSE® process
Double effect evaporation	
Triple effect evaporation	DEMEX process

percent and 40 to 50 percent of the energy of a single stage flash vaporization for solvent recovery [2]. These reductions in energy are obtained because the heat required to vaporize the solvent in the higher pressure flash vaporization stages is used to vaporize solvent in the next lower pressure flash vaporization stages. The amount of energy saved is proportional to the solvent-to-feed ratio and the cost of steam, fuel and electrical power [2].

B. Supercritical Solvent Recovery

Supercritical solvent recovery methods are also being used in some deasphalting and demetallization processes. The Kerr-McGee Residual Oil Supercritical Extraction (ROSE®) and the UOP Demex processes are two of the processes for which considerable information has been published [3,6,10,11,14]. The process flows for these processes are presented in Figures 4.15 and 4.16.

The process flow of the supercritical solvent recovery processes are very similar and consist of mixing the feed with solvent and separating an asphalt rich phase which flows through a heater and stripper for recovery of the solvent in the usual manner of a conventional deasphalting unit. The extract solution of DA oil and solvent is pumped from the settler or first extractor, is heated, and enters the resin settler for separation of the resins. The resins are pumped to a stripper for recovery of the solvent. The extract, DA oil-solvent, solution is pumped through a heater wherein it is heated above the critical temperature and passes into a settler for separation of the DA oil and solvent as separate liquids. The liquid solvent is cooled by heat exchange with the extract solution and recycled in the process. The DA oil leaving the DA oil separator is pumped to a stripper for removal of the residual solvent by steam stripping as is done in a conventional deasphalting unit. The solvent contained in the resins and asphalt from the separators are recovered using the conventional flash and/or stripping operations. The vapors from the strippers are cooled to condense the water; the solvent vapors are compressed and recycled in the process.

V. DEASPHALTING DEVICES

The deasphalting devices used in continuous deasphalting units consist of vertical towers containing slats, gratings, baffles or rotating discs and stators [1,2]. The use of baffle towers were the first replacement for the mixer–settlers used in the early deasphalting units. The Rotating disc contactor, RDC, was first introduced by Shell for the furfural extraction of lubricating oil base stocks. It has also been applied to deasphalting of residua and heavy vacuum gas oils for manufacture of base oils and feedstocks to fluid catalytic cracking units. A sketch of a rotating disc contactor is shown in Figure 4.17 [2].

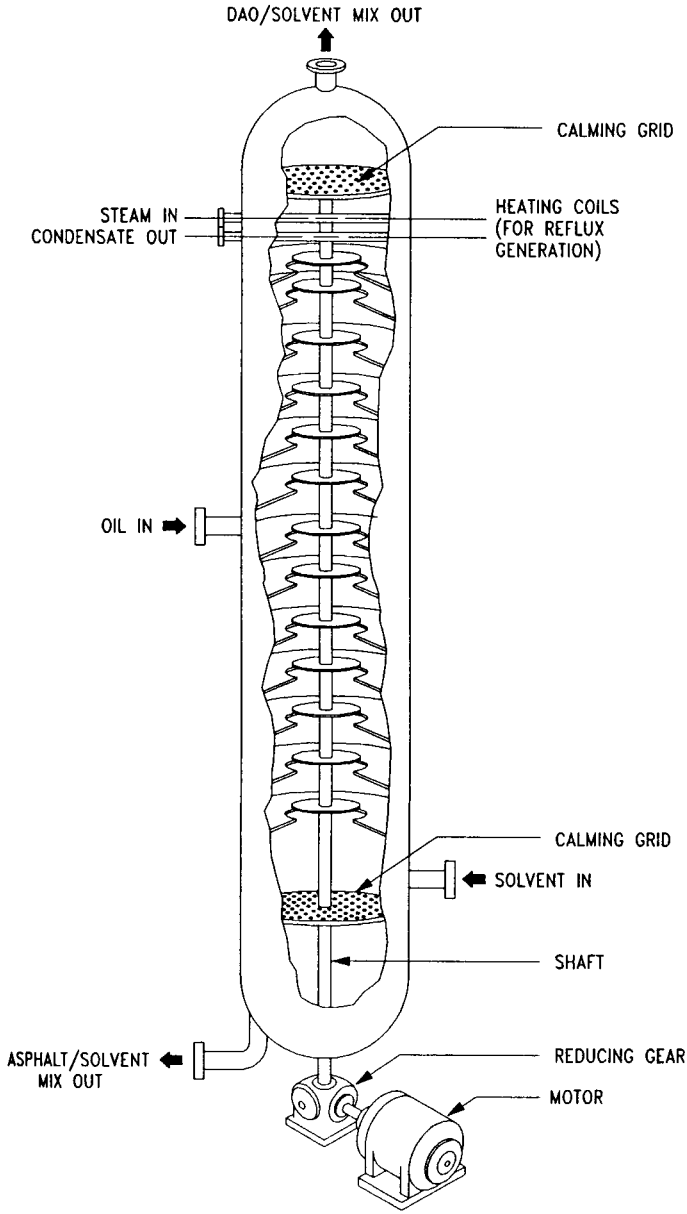

Figure 4.17 Rotating disc contactor. Reprinted from Ref. [2] by courtesy of Foster Wheeler Corporation.

Design of deasphalting devices are proprietary to licensors of the processes. They are based on pilot plant data and data from existing commercial units. The maximum throughput of the RDC is a function of the specific energy input of the rotating disc, solvent and feedstock. Published information comparing pilot plant and commercial RDCs are presented in Figure 4.18 [15] which compares specific energy input and throughput.

Specific energy input = $E = N^3R^5/HD^2$ in $ft^2/second^2$

where D = Tower diameter, ft

H = Height of a compartment, ft

N = Rotor speed, revolutions per second

R = Diameter of the rotor, ft

Tower capacity = $T = V_D V_C/C_R$ in ft/hour

where V_D = Superficial velocity of the solvent, ft/hr

V_C = Superficial velocity of the residua, ft/hr

C_R = RDC constricting factor, the smaller of S^2/D^2 or $(D^2 - R^2)/D^2$

S = Inner diameter of the stator, ft

R = Diameter of the rotor, ft

The maximum throughput at flooding is given at constant solvent to feed ratio as a function of the energy input as depicted in Figure 4.17 which compares operation of a pilot plant RDC and a commercial RDC for propane deasphalting in lubricating oil manufacture [15].

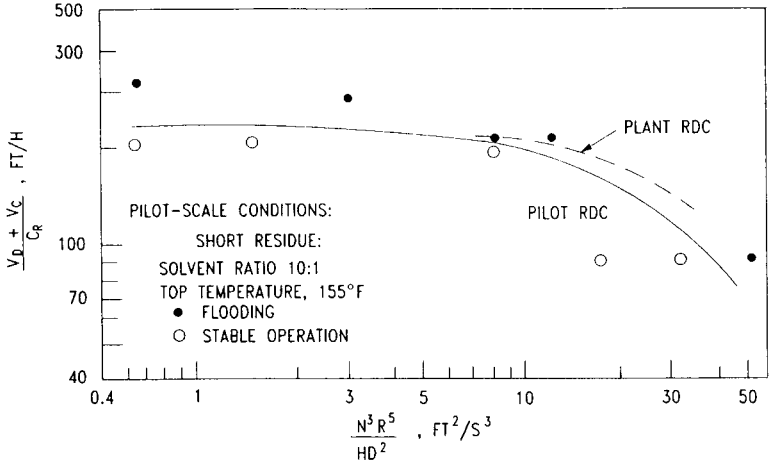

Figure 4.18 RDC capacity for propane deasphalting. Reprinted from Ref. [16] by courtesy of *Oil and Gas Journal*.

VI. INVESTMENT AND UTILITY REQUIREMENTS [2,9,17]

Investment and utility requirements are site specific and vary widely depending on unit feed capacity, solvent-to-feed ratio, feedstock quality and product quality. Since the solvent-to-oil ratios are higher for bright stock manufacture than for preparation of cracking feedstocks, the investment and utility costs will also be higher for the bright stock deasphalting units. Accurate investment and operating costs can therefore only be determined by a detailed design and definitive estimate for the particular feed and product to be manufactured. Investment and utility requirements for various deasphalting processes are available from licensors with some information being published on a biannual basis in *Hydrocarbon Processing*.

A typical set of utility requirements reported by Foster Wheeler [2] are summarized in Table 4.9 for a dual effect solvent vaporization type unit. Kerr-Mcgee [11] reports that the utility consumption for a supercritical solvent recovery unit is less than for that of a conventional single effect solvent vaporization recovery system. These data are summarized in Table 4.10 [11].

The relative energy costs for multiple effect and supercritical solvent recovery reported by Nelson [11] are summarized as follows.

Solvent recovery technique	Relative energy cost
Single-effect evaporation	280
Double-effect evaporation	170
Triple-effect evaporation	150
(Supercritical) ROSE™	100

This information indicates that the utility requirements for use of supercritical solvent recovery are less than that for the use of double or triple effect evaporation for propane deasphalting.

Table 4.9 Typical Utility Requirements for Solvent Deasphalting Using Double-Effect Solvent Vaporization

Per barrel of feed	Lube oil	Cracking stock
Fuel liberated, BTU (LHV)	86,000	89,000
Power consumption, KWH	2.1	2.0
Steam consumption (150 psig), lbs	115	60
Cooling water (250 °F rise), gal	300	Nil

Reprinted from Ref. [2] by courtesy of Foster Wheeler Corporation.

Table 4.10 Comparison of Utility Requirements for Deasphalting Supercritical versus Single-Effect Evaporation

Utility cost, $/cubic meter	Single effect	Supercritical
Fuel	3.43	5.02
Power	0.66	0.63
Steam	5.92	0.28
Total	10.01	4.09
Basis		
Solvent	Propane	
Solvent-to-oil ratio	10–12:1	
Fuel	$0.006/MJ	
Steam	$0.018/KG	
Electric power	$0.050/KW	

Reprinted from Ref. [10] by courtesy Kerr-McGee Corporation.

Table 4.11 Solvent Deasphalting Utility Comparison for Deasphalting Double-Effect Evaporation versus Supercritical

Utility consumption, $/day	Double effect	Supercritical
Fuel	9,072	10,865
Power	12,007	11,952
Steam	2,901	1,800
Total	23,980	24,617
Basis		
Capacity	20,000 BPSD Arabian heavy residuum	
Solvent	n-butane	
Solvent to feed ratio	Moderate	
Fuel	$4.50/MMBTU (LHV)	
Steam	$5.70/1000 lbs	
Electric power	$0.045/KW	

Reprinted from Ref. [2] by courtesy of Foster Wheeler Corporation.

Table 4.12 Solvent Deasphalting Investment and Utility Costs

	Double-effect		Supercritical
Capacity, BPSD	15,000–2,000		30,000
Investment, U.S. $/bbl	8–92 1,530–7,800		4qr/89 1,000
U.S. Gulf Coast, 03/93	1,550–7,900		1,085
Utilities per barrel of feed	Base Oil	Cracker	
Fuel, 1,000 BTU	86	89	80–110
Power, kWh	2.1	2.0	2.0
Steam, 150 psig, lbs	115	60	12
Cooling water, (25°F rise),			

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Foster Wheeler [2,16] has reported that utility consumption for a supercritical solvent recovery unit is essentially the same as that for a double-effect solvent vaporization recovery system. These estimates are summarized in Table 4.11 [2].

The reasons for the differences in the energy requirements reported in Table 4.11 and the comparison previously provided are not apparent. However, it is expected that the differences are related to the feedstocks used and differences in heat exchange employed in the design comparisons.

Table 4.13 Deasphalting Unit Energy Reductions Economics

	Number of evaporation stages		
U.S. Gulf Coast, January, 1983	Single	Double	Triple
Conversion investment, $ [1]	0	696,000	1,040,000
Annual utility costs			
MP steam, $5.65/1000 lbs	141,100	141,100	141,100
LP steam $4.80/1000 lbs	1,442,500	720,300	584,500
Power, $4.80/KW	218,400	218,400	218,400
Cooling water, $0.60/1000 gal	76,800	42,000 34,600	
Fuel, $4,30/million net BTU	93,900	93,900	93,900
Total annual cost	1,972,700	1,215,700	1,072,500
Annual utility reduction	0	757,000	900,200
Payout before taxes, years	—	0.9	1.2

[1] 1700 BPSD vacuum residue, 93 % DA oil yield, 350 days/year

Reprinted from Ref. [2] by courtesy of Foster Wheeler Corporation.

Investment costs for deasphalting are considerably higher for deasphalting bright stock feeds as compared to feedstock to cracking units. Investment costs also depend on the feedstock and product quality, solvent recovery technique and solvent or solvents used. Investment and utility requirements reported in *Hydrocarbon Processing* [17] are summarized in Table 4.12. These data were updated using the Nelson Cost Index for refinery construction. The lower value should be used for estimating costs of units used to prepare cracking feedstocks and the higher value for units used to prepare bright stock feeds because deasphalting units used to prepare deasphalted oils for base oil manufacture are usually considerably smaller than those used to prepare feedstocks for fuels processing units.

Investment costs for conversion of a single-effect evaporation solvent recovery system to a two- and three-stage solvent recovery system are summarized in Table 4.13 [2]. These data show that the payout for adding a two-stage unit is lower than the addition of a three-stage solvent recovery system. However, the data show that there is a good payout for increasing the number of evaporation stages.

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ADDITIONAL READINGS

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5

Solvent Refining of Lubricant Base Oil Stocks

I. INTRODUCTION

Petroleum refiners introduced solvent extraction in the late 1920s and early 1930s as an alternative to chemical and clay treating for the removal of undesirable constituents and for improving the viscosity index of lube base stocks. Extraction has also been used to improve the quality of naphthene pale oils and is now being used to reduce the toxicological aggressiveness of these base oils. More recently the Texaco MP Lube Oil Refining Process and the EXOL N Refining Process based on the use of N-methyl-2-pyrrolidone (MP) as the extraction solvent have been developed. These processes are being used as a replacement for furfural and phenol in the extraction of lube oil base stocks. A discussion of the lube solvent extraction processes and a comparison of the major extraction solvents (furfural, MP and phenol) are provided later.

The feedstocks and products of the solvent refining processes are listed in Table 5.1 The products are the streams used for the manufacture of lubricating oil base stocks. The by-products from lube solvent refining processes are aromatic extracts which are used in the manufacture of asphalt, carbon black, fuel, petrochemicals, rubber and as coker and FCCU feed.

Solvent extraction is used for the purpose of removing aromatics and other undesirable constituents to improve the VI and quality of lube base stocks. A summary of the major effects of solvent extraction on the properties of lube base stocks is presented in Table 5.2.

Table 5.1 Solvent Refining Feedstocks and Products

Feedstocks	Products
Paraffinic distillates	Paraffinic raffinates
Deasphalted oils	Bright stock raffinates
Hydrotreated oils	Lube oil raffinates
Naphthenic distillates	Naphthenic raffinates
Cycle oils	Medium VI raffinates

Petroleum refiners have devoted a considerable amount of time and effort to the search for a lube extraction solvent which will meet the characteristics listed in Table 5.3. Although no solvent meets these requirements entirely, several solvents have been identified and patented and of those identified only those listed in Table 5.4 have been used commercially [1,2].

MP, furfural and phenol are the only solvents used to any great extent with furfural being the solvent of choice on a worldwide basis. The liquid sulfur dioxide and the Duo-Sol processes are still used to a minor extent. Chlorex was never used very extensively. However, it is currently being used to extract lube base stocks in at least one plant in Eastern Europe.

II. PROCESSES

A. The Duo-Sol Process [1,3,4,5]

The Duo-Sol process is the only double-solvent process used to both deasphalt and extract lubricating oil feedstocks. Since it is both a deasphalting and extraction (refining) process, it does not conveniently fit into either the deasphalting or refining processes used for the manufacture of lube oils and is being included here as a matter of information. Propane is used as the deasphalting or paraffinic solvent and "Selecto" (a mixture of phenol and cresylic acid) is used as the extraction solvent in this process. A simplified flow

Table 5.2 Solvent Extraction Effects on Lubricant Feedstocks

Increases viscosity index	Reduces viscosity
Improves oxidative stability	Reduces aromatic content
Increases wax content	Increases pour point
Improves thermal stability	Reduces carbon residue
Improves inhibitor response	Reduces sulfur content
Improves color	Reduces nitrogen content
Reduces toxicity	Reduces specific gravity

Table 5.3 Characteristics of an Ideal Extraction Solvent

High selectivity for undesirable constituents
Good solvent power; low solvent-to-oil ratios
High extraction temperature; good mass transfer
Easy recovery; simple flash distillation
Low vapor pressure: avoid use of pressure equipment
High density; rapid phase separation
No emulsification; rapid phase separation
Good stability; no chemical or thermal degradation
Adaptable to a wide range of feedstocks
Available at reasonable cost
Non-corrosive to conventional metals of construction
Non-toxic; environmentally safe

Reprinted from Ref. [2] by courtesy of Texaco, Inc.

diagram of the Duo-Sol Process and the mixer–settlers used are shown in Figures 5.1, 5.2 and 5.3 [5].

The main application of the "Duo-Sol" process is in the manufacture of bright stocks from vacuum residua. The process variables are temperature, solvent composition and solvent dosage. Extraction is conducted in seven- to nine-batch extractors which are connected end to end followed by solvent recovery conducted in multistage flash vaporization and stripping towers.

The product is a raffinate which requires no solvent or hydrogen refining for the manufacture of lubricating oil base stocks. Dewaxing of paraffinic feedstocks is required and finishing may be required for base oils derived from some crude oils or for the manufacture of certain lubricating oils. Solvent dosages range from 100 to 400 percent "Selecto" and 150 to 500 percent propane basis feedstock. The temperature and solvent dosage used and yields of refined oil are highly dependent (like all refining processes) on the crude source being used and the quality of the base stock being manufactured. The selectivity of this process is excellent because propane dissolves some of the more paraffinic components which are normally extracted by the single solvent

Table 5.4 Commercially Used Lube Extraction Solvents

N-Methyl-2-pyrrolidone	Duo-Sol (phenol–cresylic acid–propane)
Furfural	Chlorex (β,β,dichloroethyl ether)
Phenol	Nitrobenzene
Sulfur dioxide	Sulfur dioxide–benzene

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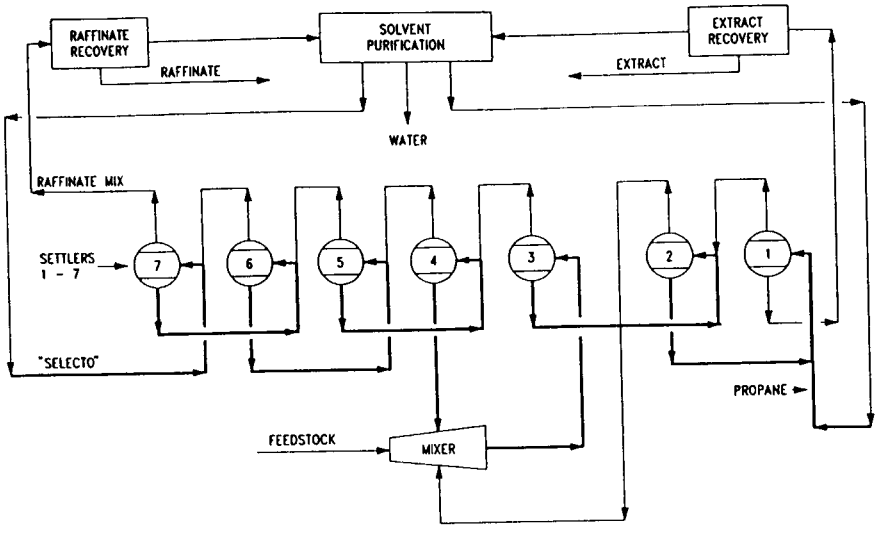

Figure 5.1 Duo-Sol process flow diagram.

refining processes. Since this process is capital-intensive and phenol is toxic, no new units have been built since the mid 1950s.

B. The Edeleanu Process [1,6]

The Edeleanu Process based on the use of liquid sulfur dioxide was the first extraction process used by the petroleum industry and was first introduced in 1907 to reduce the smoke point of kerosene. It was later applied to the extraction of lubricating oils and has been used in combination with benzene for the extraction and dewaxing of lubricating oil base stocks. A simplified flow diagram for this process is shown in Figure 5.4

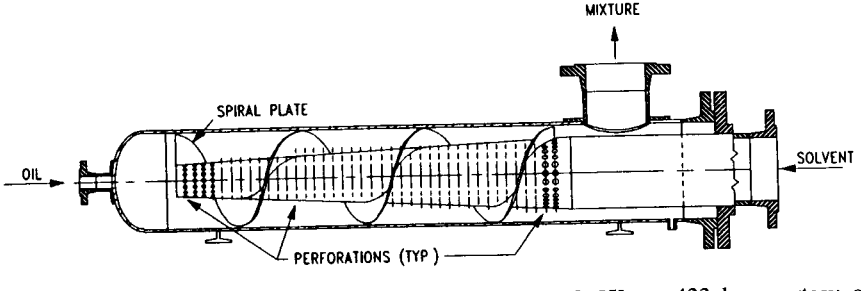

Figure 5.2 Duo-Sol crude mixer. (Reprinted from Ref. [5], p. 433 by courtesy of McGraw-Hill Book Co.)

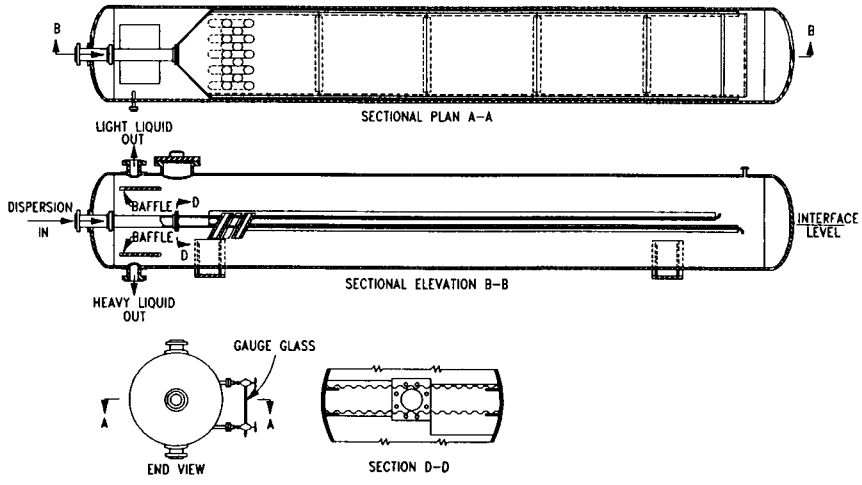

Figure 5.3 Settler for the Duo-Sol Process. (Reprinted from Ref. [5], p. 443 by courtesy of McGraw-Hill Book Co.)

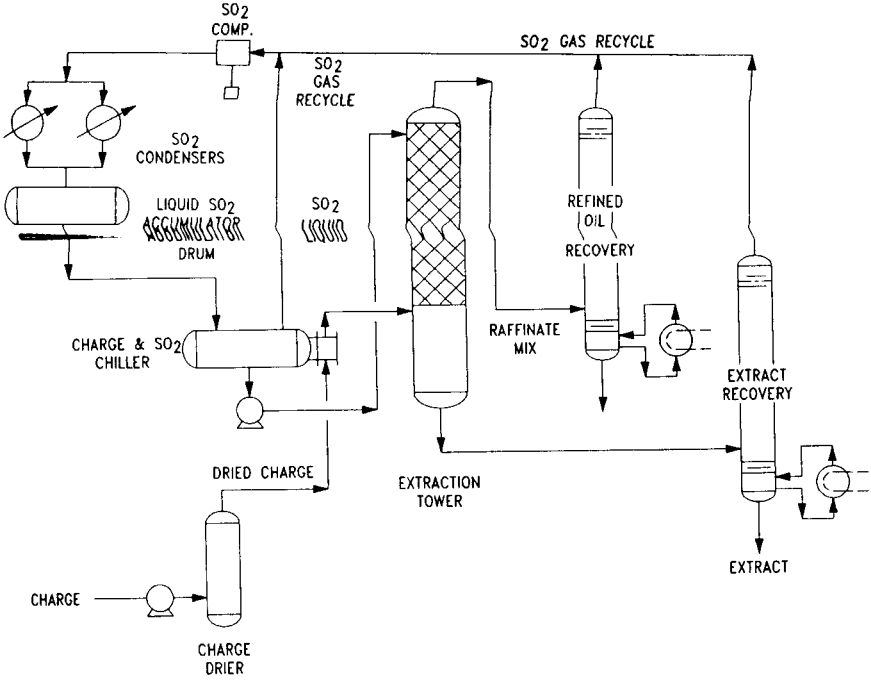

Figure 5.4 Liquid sulfur dioxide extraction process flow.

The water content of the oil is reduced to less than 0.005 weight percent in a vacuum dehydrator, then mixed with liquid SO_2 and cooled by autorefrigeration before being introduced into the extraction (packed) tower where it is countercurrently contacted with dry solvent which selectively removes some of the aromatics, nitrogen and sulfur present in the feedstock. The raffinate mix (oil rich phase) and extract mix (solvent rich phase) are removed at the top and bottom of the extraction tower, respectively. Liquid SO_2 is removed from these streams through the use of multi-stage evaporation. The SO_2 is recovered using water-cooled condensers, compressed and recycled in the process. The water content of the solvent is controlled by passing a portion of the SO_2 through a drying tower.

Although liquid SO_2 has good solvent power and selectivity for aromatic compounds, the requirement for low extraction temperatures limits its use to the extraction of naphthenic and low pour or dewaxed paraffinic feedstocks. The disadvantages for use of liquid SO_2 are 1) toxicity, 2) air pollution, 3) moisture control to prevent corrosion and 4) maintenance costs related to these items. No new units have been built for extraction of lube oils since the late 1950s. Although there are still some units in operation in Europe, currently the process is being used at only one location in the United States for the extraction of naphthene oils.

C. The Furfural Refining Process [1,2,7,8,9]

The furfural refining process is the most widely used process for the refining of lube oil base stocks. It was first used commercially at the Texaco Lawrenceville, IL Plant in 1934. Although Shell held the original patents for the use of furfural, the process has been most extensively developed and licensed by Texaco [1]. This process has also been used for the extraction of straight-run gas oils and light- and heavy-cycle oils from catalytic cracking operations [1,7].

In addition to the quality of the feedstock, the main process variables are temperature, solvent dosage, purity of the solvent and the quantity of extract recycled to the feed or below the feed in the extraction device. The yield of refined oil (selectivity) of furfural is equivalent to or better than that of the other single solvents currently in use. The temperatures and solvent dosages used are highly dependent on the quality of the feedstock crude source and the quality level of base stocks being produced. Although the normal ranges are 100 to 250°F and 100 to 500 volume percent furfural basis feed, higher and lower temperatures and dosages are used in some cases.

A simplified flow diagram for a furfural refining unit is shown in Figure 5.5 [9]. The feedstock is contacted countercurrently in an extraction device which preferentially extracts some of the aromatics and oxygen, nitrogen and sulfur compounds from the feedstock. The solvent-to-oil ratio used depends on the feedstock quality, temperature of the extraction and desired base oil quality.

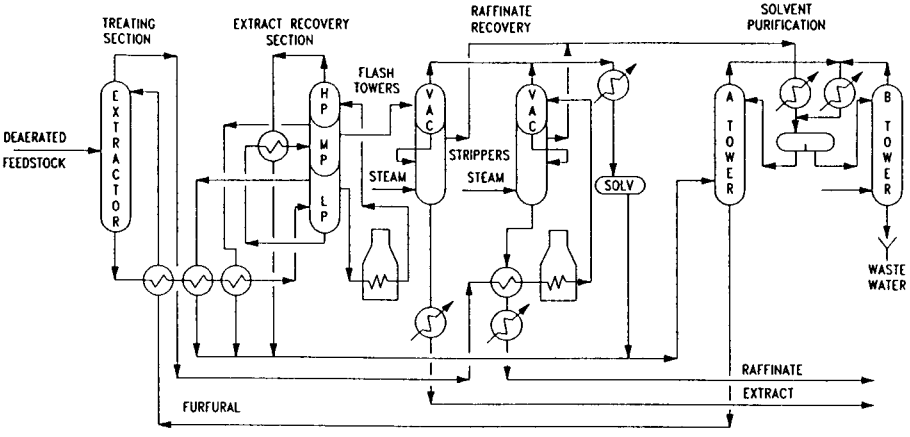

Figure 5.5 Texaco Furfural Refining Process. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

The raffinate and extract leave the top and bottom of the extractor, respectively, and the solvent is removed by multiple effect evaporation and steam stripping. The water which enters the process is removed by azeotropic distillation and the solvent is recycled in the process. Aromatic content of the extract can be increased and controlled by cooling and settling of the extract–solvent mix. The resulting cycle oil or pseudo-raffinate which is produced can be recycled to the feed or extracted separately to increase refined oil yield. Alternately, this cycle oil can be further processed to produce medium VI base stocks or used as FCCU feedstock.

Although many other extractors have been used successfully in the laboratory for furfural refining of lube oil base stocks, the extractors currently being used are packed towers, rotating disc contactors (RDC) and centrifugal contactors. RDCs are the currently favored extraction devices because of their excellent turn-down ratios, rapid changeover of feedstocks and the elimination of the need to shutdown for cleaning (decoking) which is experienced with packed towers. Centrifugal contactors are excellent extractors and have the least holdup of the devices being used but require considerably more maintenance than RDCs or packed towers.

Although several new furfural refining units have been brought on-line in recent years and some new units are under construction or in the planning stage, the last grassroots furfural refining unit in the United States was brought on line in 1977. Several furfural refining units have been converted to Texaco MP Refining Units and conversion of additional units is under consideration.

D. N-Methyl-2-Pyrrolidone (MP) Refining Processes

Although Texaco obtained the first patents for the use of MP for the refining of lubricating oils, the first commercial unit was installed in Fawley, England by Exxon [10]. Processes based on the use of MP are licensed by Exxon (EXOL N Extraction) and Texaco Development Corporation (Texaco MP Refining Process). The process flow for a Texaco designed MP Refining Unit is shown in Figure 5.6. The process flow for the Exxon designed units are shown in Figures 5.7 and 5.8.

The flow for these processes is similar to that of the furfural refining and phenol refining processes. The Exxon licensed units follow the phenol design and the Texaco units follow the furfural or phenol designs. Texaco favors the furfural design for ground up units and retains most of the phenol design for conversion of phenol units. Exxon uses essentially the phenol designs for ground-up units and conversion of phenol units. The main differences between these processes are the different methods used in the recovery and drying of the solvent; the use of wet MP in the Exxon Exol N Process and the preference for anhydrous MP in the Texaco MP Refining Process. Cooling and/or water injection into the extract mix leaving the extractor can be used to produce cycle oils for manufacture of medium VI base oils and to control the aromatic content of the extract. The extraction devices used are packed towers, trayed towers and RDCs [2,12,13,14,15].

N-methyl-2-pyrrolidone (MP or NMP) is a highly selective and non-toxic solvent. In addition to the quality of the feedstock, the main process variables

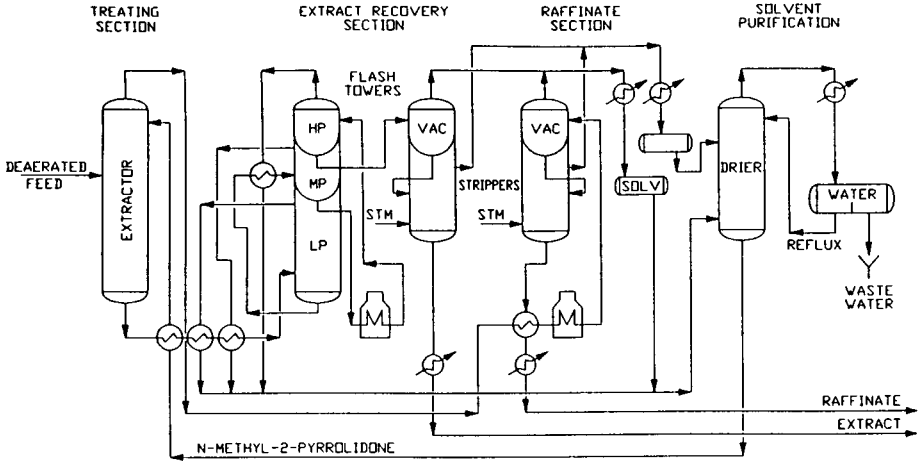

Figure 5.6 Texaco MP Refining Process flow diagram. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

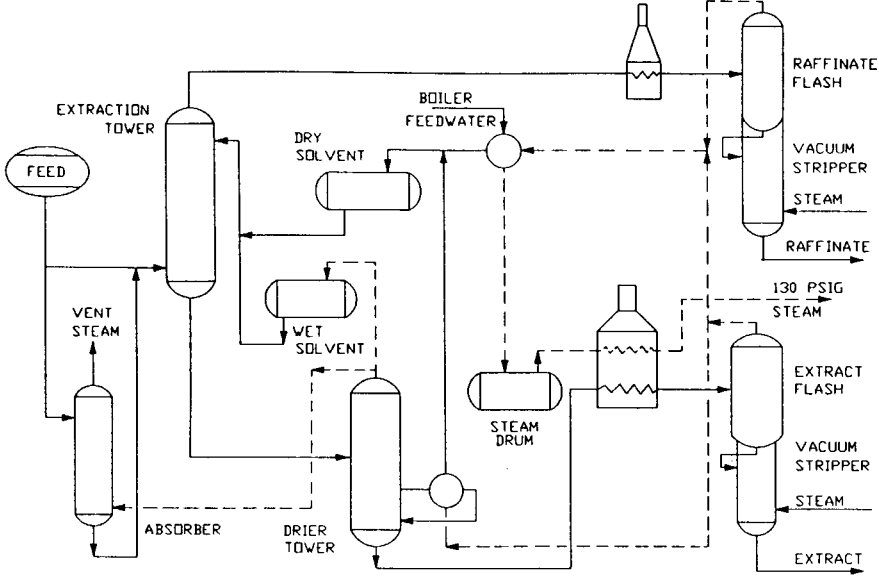

Figure 5.7 Exol N Extraction Unit using steam stripping. (Reprinted from Ref. [12] by courtesy of Exxon Research and Engineering Co.)

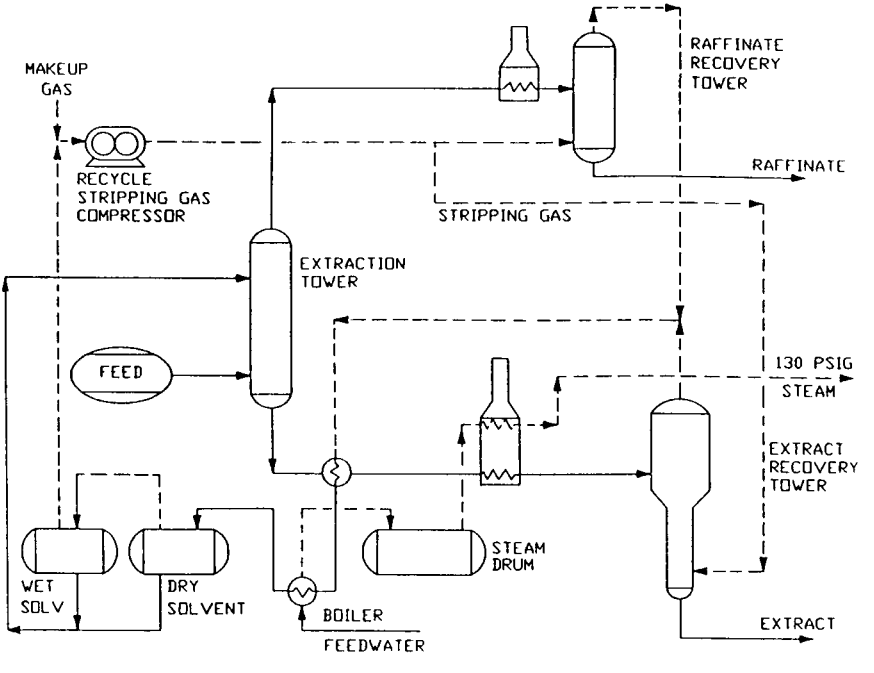

Figure 5.8 Exol N Extraction Unit using inert gas stripping. (Reprinted from Ref. [12] by courtesy of Exxon Research and Engineering Co.)

are temperature, dosage, purity of the solvent and the amount of water or wet solvent injected into the feed or into the extraction device below the feed. MP has better solvent power than either furfural or phenol and selectivity which is equivalent to furfural and better than phenol with most feedstocks. Although the water content of the solvent should be minimized to maximize solvent power and minimize the solvent circulation, there are some feedstocks (crude source dependent) where injecting water in the solvent, feedstock or extractor is used to improve the selectivity of MP.

Temperature has a greater effect on the selectivity and solvent power of MP than with other solvents. Since the limitations in most lube refining units is solvent turnover, increases of 25 to 60 percent in feed rate have been obtained from the conversion of furfural and phenol refining units to MP [9,12,14,16].

The investment, operating and energy costs are lower for the use of MP as compared to the use of furfural or phenol because the higher solvent power (lower treating dosage) of MP results in the need for smaller units and less energy consumption for a given size lube plant. Comparative investment costs and utilities consumption for the use of furfural and MP are shown in Table 5.5 [17].

E. The Phenol Refining Process

The phenol refining process was first used for the extraction of lubricating oil feedstocks by Imperial Oil of Canada in 1930 and was most extensively licensed by Kellogg under the patent rights of Exxon, Unocal, Standard Oil of Indiana and Kellogg [1,18]. Phenol is a highly toxic solvent. The selectivity of phenol is good but lower than that of furfural or MP. In addition to the quality

Table 5.5 Investment Cost and Utilities Requirements Grass Roots Furfural and MP Refining Units

U.S. Gulf Coast 1991	Furfural	MP
Feed rate, BPOD	10,000	10,000
Investment		
On-site facilities, M$ U.S.	13,000	11,300
Solvent inventory, M$ U.S.	380	385
Energy consumption/bbl feed		
15 psig steam, pounds	0.38	0.0
40 psig steam, pounds	10.3	5.0
Fuel, MBtu	109	96
Electricity, kWh	0.91	0.69
Energy consumed, MBtu/bbl feed	133	110

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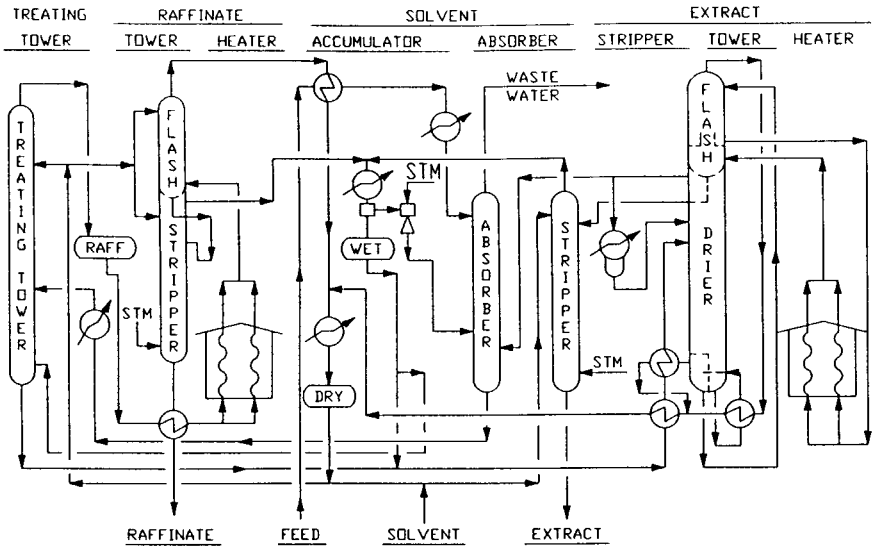

Figure 5.9 Phenol refining unit flow diagram. (Reprinted from Ref. [2] by courtesy of Texaco, Inc.)

of the feedstock, the main process variables are temperature, dosage, the quantity of water or oil in the circulating solvent and the dosage of wet solvent or water injected into the feed or extractor below the feed point. The process flow for a phenol refining unit is shown in Figure 5.9 [14].

It should be noted that some phenol units are used to generate low pressure steam. Some units also use inert gas rather than steam for removing the last traces of phenol from the raffinate and extract. In these cases the process flow is like that for the EXOL N extraction process shown in Figures 5.8. No new phenol refining units have been brought onstream for several years and some refiners have converted phenol units to the use of MP or replaced them with furfural or MP refining units.

F. Comparison of Major Solvent Refining Processes

The information presented in Table 5.6 (estimated from the NPRA annual survey of lube refiners) shows that MP replaced furfural and phenol as the extraction solvent of choice in the USA and Canada in the short period of one decade. The reasons MP replaced phenol rather than furfural at such a rapid rate are related to (1) the environmental movement and refiners' desire to eliminate the use of the highly toxic phenol and (2) the ease with which a phenol unit can be converted to MP.

Table 5.6 Relative Use of Lube Extraction Processes

Approximate percentage for USA and Canadian lube plants					
Solvent	1975	1980	1985	1990	1993
Furfural	40	42	38	33	33
N-Methyl-2-pyrrolidone (MP)	0	23	42	53	52
Phenol	40	20	10	5	6
Duo-Sol and sulfur dioxide	20	15	10	9	9
Total thousand BPCD	355	381	368	359	334

The chemical structures of the three major lube extraction solvents in use today are shown in Figure 5.10 and the physical and chemical properties for these solvents are presented in Table 5.7. Although there are some properties which favor the use of one solvent over the other, MP, which costs the most, is the most cost-effective solvent due to its high solvent power and selectivity.

The higher boiling point of MP provides better heat integration than does the boiling point of the other solvents. The higher specific gravity and lower boiling point of furfural are advantages with the lower boiling point being desirable when processing low boiling feedstocks such as transformer oil distillates.

Although the heat of vaporization is higher per pound of solvent for MP, it is lower per unit volume which is the normal basis used to measure solvent dosage. The higher MP content of the raffinate phase requires slightly more energy to recover a given volume of raffinate and considerably less energy to recover the solvent in the extract recovery section. The extract recovery section is usually the limitation in most extraction units.

Table 5.7 Properties of Major Lube Extraction Solvents

	Furfural	MP	Phenol
Density, 25/4°C	1.15	1.03	1.07
Boiling point, °F	323	395	359
Melting point, °F	−37	−12	106
Heat of vaporization			
BTU/pound @ 760 mm Hg	194	212	206
BTU/gallon @ 760 mm Hg	1625	1537	1547
Viscosity, cP at 140°C	0.95	1.02	2.58
Specific heat, BTU/pound at 130°F	0.42	0.42	0.56

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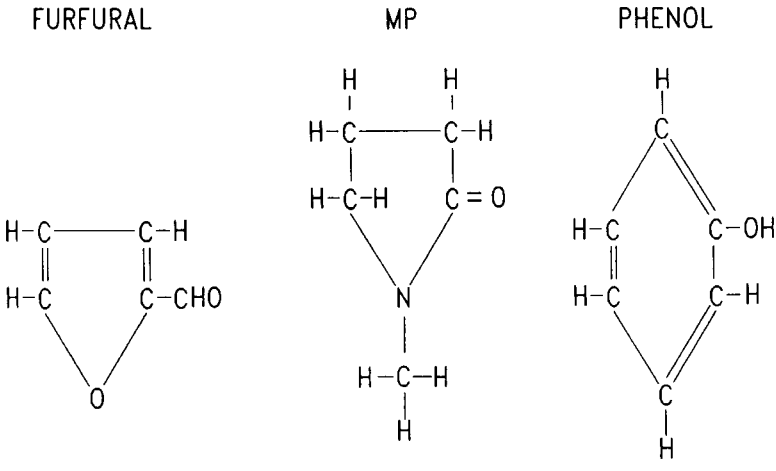

Figure 5.10 Chemical structure of major lube extraction solvents.

The information tabulated in Tables 5.8 to 5.10 show that each solvent offers advantages over the other. Furfural offers advantages in selectivity, emulsibility, settling time and coalescence. MP is best as regards solvent power, stability and toxicity.

Although the cost of phenol is less than that of either furfural or MP, the investment and maintenance costs are higher because of precautions which must be taken to protect personnel and the environment.

Biodegradability studies and commercial experience have shown that the major solvents pose no problems in a diversified refinery wastewater treating system. Table 5.11 provides a summary of the results of one study [19].

Table 5.8 Comparison of Major Lube Refining Solvents

Property	Furfural	MP	Phenol
Selectivity	Excellent	Very good	Good
Solvent power	Good	Excellent	Very good
Stability	Good	Excellent	Very good
Adaptability	Excellent	Very good	Good
Emulsibility	Low	Moderate	High
Settling time	Low	Moderate	High
Coalescence rate	High	Moderate	Low
Biodegradability	Good	Good	Good
Toxicity	Moderate	Low	High

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Table 5.9 Comparison of Major Lube Refining Processes

	Furfural	MP	Phenol
Solvent dosage	Highest	Lowest	Intermediate
Extraction temperature	Highest	Lowest	Intermediate
Refined oil yield	High	High	Low
Product color	Good	Best	Good
Corrosiveness	Moderate	Moderate	Moderate
Heat integration	Good	Best	Intermediate

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Table 5.10 Cost Comparison of Major Lube Refining Processes

	Furfural	MP	Phenol
Solvent, relative	1.0	2.3	0.60
Investment	Medium	Low	High
Maintenance	Medium	Low	High
Energy	High	Low	Medium

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Table 5.11 Rates of Solvent Degradation

	MP	Phenol	Furfural
Static test with acclimated activated sludge culture	0.022	0.056	0.018
Static test with non-acclimated activated sludge culture	0.012	0.009	<0.001
Continuous activated sludge tests, average	0.015	0.020	0.017

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Table 5.12 Refining Process Variables

Crude source	Solvent dosage
Feedstock	Solvent purity
Solvent	Extractor
Temperature	Extract recycle

The rates reported in Table 5.11 were calculated using the following equation:

$$\text{Rate} = \frac{\text{TOC Removed (mg/L)}}{\text{Reaction or Retention Time(hr)} \times \text{MLSS(mg/L)}} \quad (1)$$

Where: TOC is the total organic carbon

MLSS is the nominal mixed liquor suspended solids.

The results of this study show that the solvents are readily biodegradable in acclimated sludge units and that concentrations as high as 1000 ppm of the major solvents in waste waters can be readily handled by an acclimated waste treating unit.

III. PROCESS VARIABLES AND OPERATING CONDITIONS [9]

A listing of process variables is provided in Table 5.12. Typical operating conditions and refined oil yields are summarized in Table 5.13.

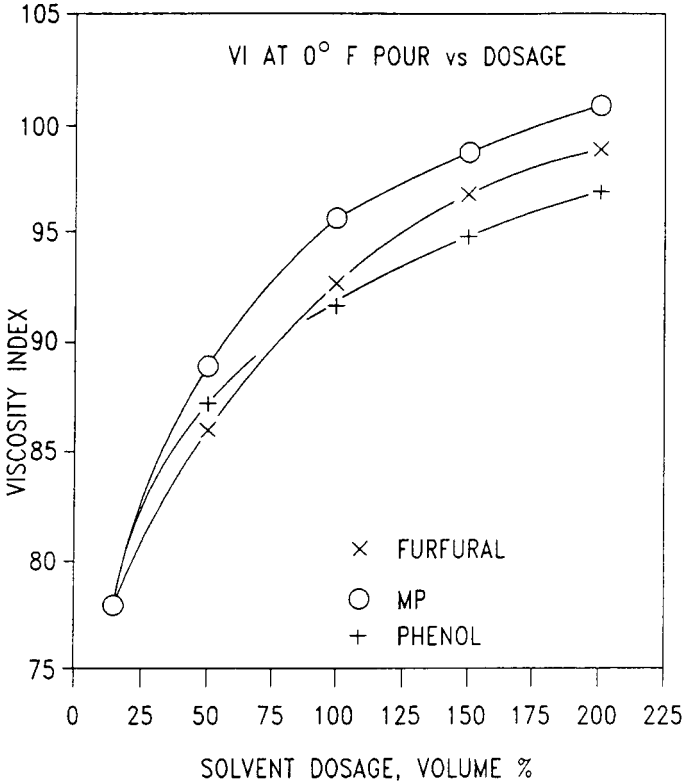
A. Effects of Solvent and Solvent Dosage [9]

The effects of solvent and solvent dosage on the yield and VI of a mid-continent 335 neutral distillate are shown in Figure 5.11. These data show that solvent dosage is lower when using MP and yield is higher when using furfural. Solvent dosage was lowest with MP in all cases. Furfural and phenol dosages were the same at the 90 VI level, lower with phenol than with furfural below 90 VI, and lower with furfural than with phenol above 90 VI. It should be noted that the same yield could be obtained at the same VI level with each of these solvents by selecting the proper processing conditions. However, the advantage in solvent dosage would be for the use of MP.

Additional data showing the effect of solvent and solvent dosage when refining a mid-continent SAE 10 distillate and deasphalted oil are shown in Figures 5.12 and 5.13. These data show that MP and furfural have a higher

Table 5.13 Solvent Refining Process Conditions

Solvent	MP	Furfural and phenol
Solvent dosage, volume %	75–400	75–600
Temperature, °F	100–190	100–250
Refined oil yield, volume %	30–90	30–90



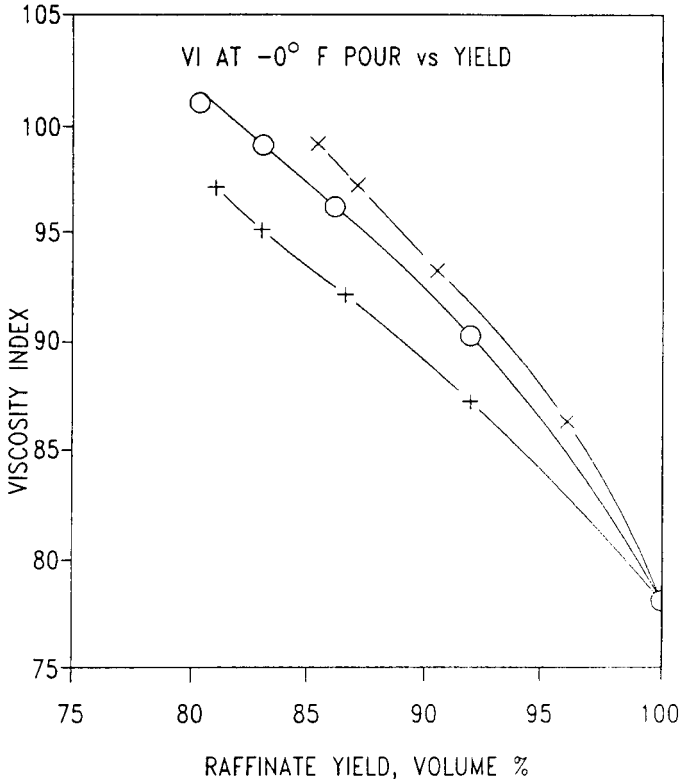


Figure 5.11 Effect of solvent and solvent dosage—335 neutral distillate SAE 10 at 95 VI & 0°F pour point. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

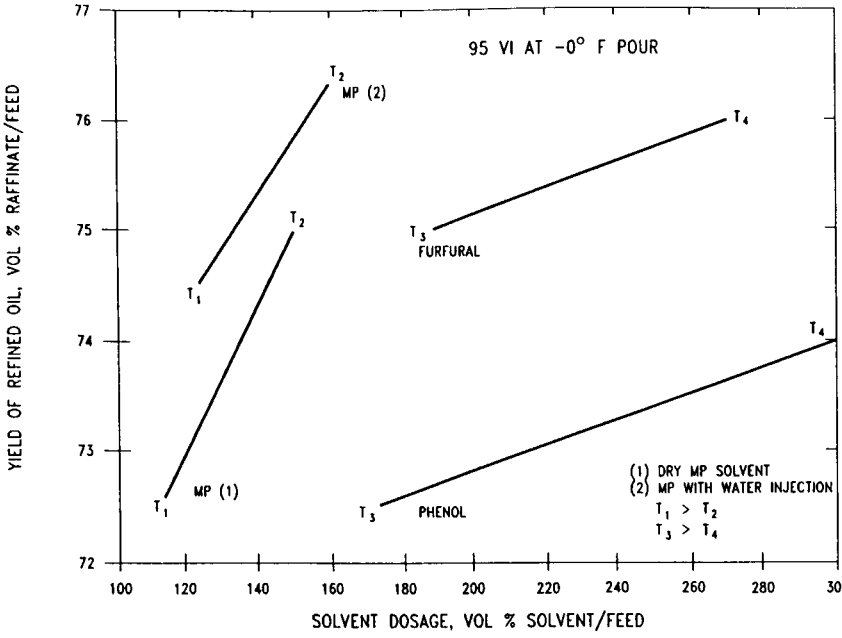


Figure 5.12 Selectivity versus solvent dosage. (Reprinted from Ref. [14] by courtesy of Texaco, Inc.)

selectivity than does phenol. The data also show that MP has a higher solvent power than either furfural or phenol.

Since the dosage required to attain a given VI base oil decreases with an increase in temperature, the data in Figures 5.12 and 5.13 clearly show that a change in temperature has a greater effect with MP as compared to either furfural or phenol.

Figure 5.14 presents a comparison of the solvent dosage requirements when refining different feedstocks with furfural, MP and phenol. These data show that the solvent dosage requirements are lower with MP than with furfural or phenol. It should also be noted that the ratios of solvent dosage requirements vary with crude sources as well as with viscosity grade.

B. Effects of Temperature and Dosage [9]

The effect of temperature and dosage for the refining of a 335 neutral distillate are shown in Figure 5.15. These data show that at a specified VI level, solvent dosage and yield decrease as the temperature is increased; that is to say that if the temperature is decreased the solvent dosage must be increased to make a product oil of the same viscosity index.

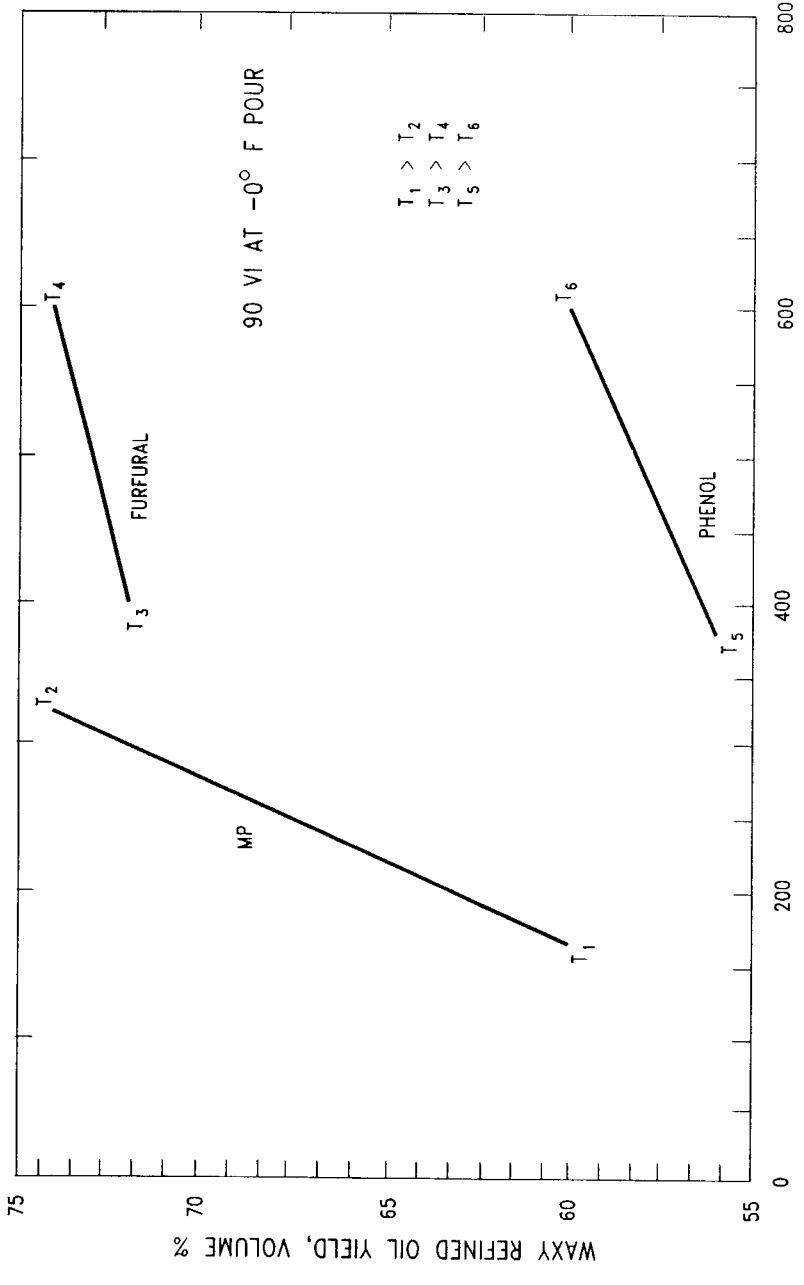


Figure 5.13 Solvent refining of deasphalted oil at 90 VI & 0°F pour point. (Reprinted from Ref. [14] by courtesy of Texaco, Inc.)

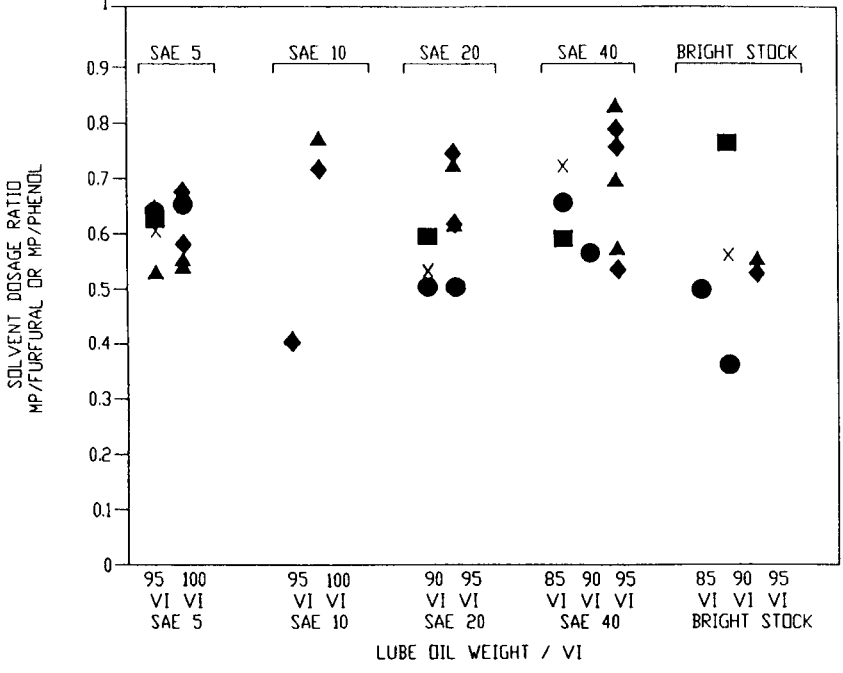


Figure 5.14 Solvent refining dosages MP versus other solvents. ■, U.S. sour (MP/furfural); ♦, U.S. M/D continent CMP/furfural); ●, U.S. coastal (MP/furfural); ▲, U.S. M/D continent (MP/phenol); X, Mideast (MP/furfural). (Reprinted from Ref. [16] by courtesy of Texaco, Inc.)

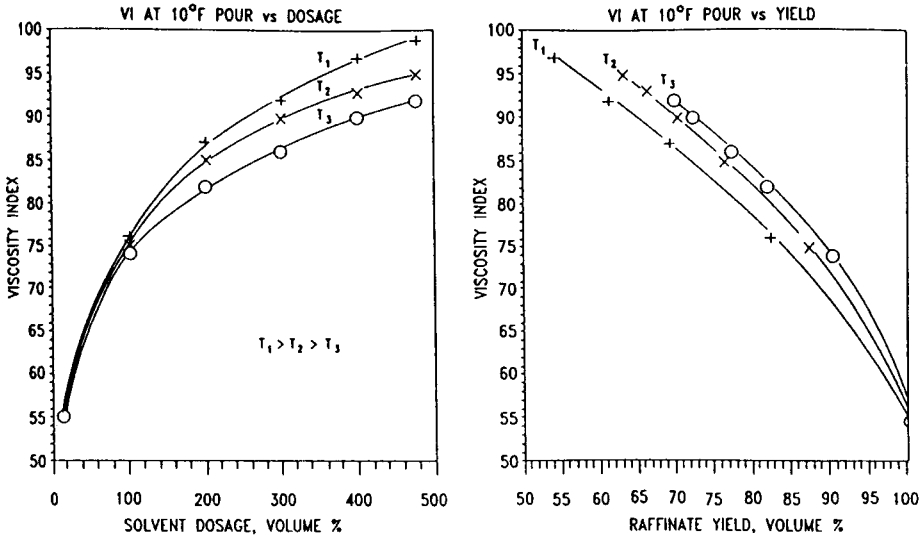

VI AT 10°F POUR vs DOSAGE
VISCOSITY INDEX
SOLVENT DOSAGE, VOLUME %
T1 > T2 > T3
VI AT 10°F POUR vs YIELD
VISCOSITY INDEX
RAFFINATE YIELD, VOLUME %

Figure 5.15 Effect of temperature on refining response of a 335 neutral distillate. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

Additional data on the effects of solvent dosage and temperature are shown in Figure 5.16. The data show that 1) temperature has a greater effect with MP, 2) solvent dosage is lower with MP and 3) the same yield of refined oil can be obtained with either solvent if the proper processing conditions are selected. The data also show that the solvent dosage advantage for use of MP increases with an increase in VI.

C. Effect of Crude Source [9]

The data shown in Figures 5.17 and 5.18 show the effect of solvent dosage on refined oil yield and base oil VI when using feedstocks from different crudes. The data in Figure 5.17 show that the yield of a given VI base oil is highly dependent on the crude source and that the VI level of the distillate cannot be used to predict refining response. The data in Figure 5.18 show that not all distillates are suitable for manufacture of base oils.

Data presented in Table 5.14 for some U.S. mid-continent distillates show that the corresponding distillate from each crude gave different results and responded differently to each solvent. The data also show that the selectivity of MP is generally equivalent to that of furfural and better than that of phenol; the solvent power of MP is better than that of either furfural or phenol.

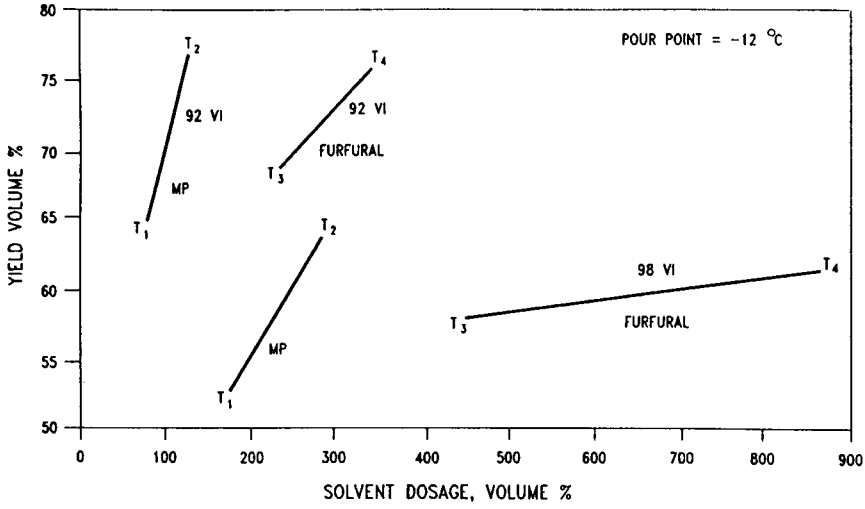


Figure 5.16 Effect of temperature and dosage—335 neutral distillate. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

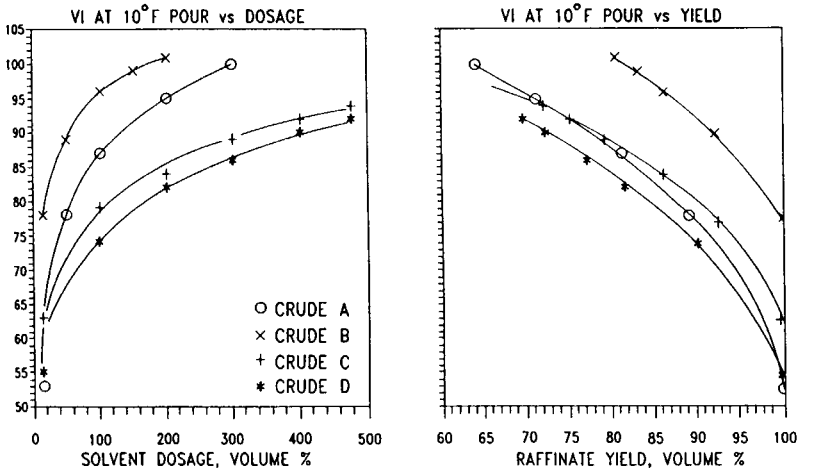

VI AT 10°F POUR vs DOSAGE
VI AT 10°F POUR vs YIELD
O CRUDE A
× CRUDE B
+ CRUDE C
* CRUDE D
SOLVENT DOSAGE, VOLUME %
RAFFINATE YIELD, VOLUME %

Figure 5.17 Refining response of 335 neutrals from different crudes. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

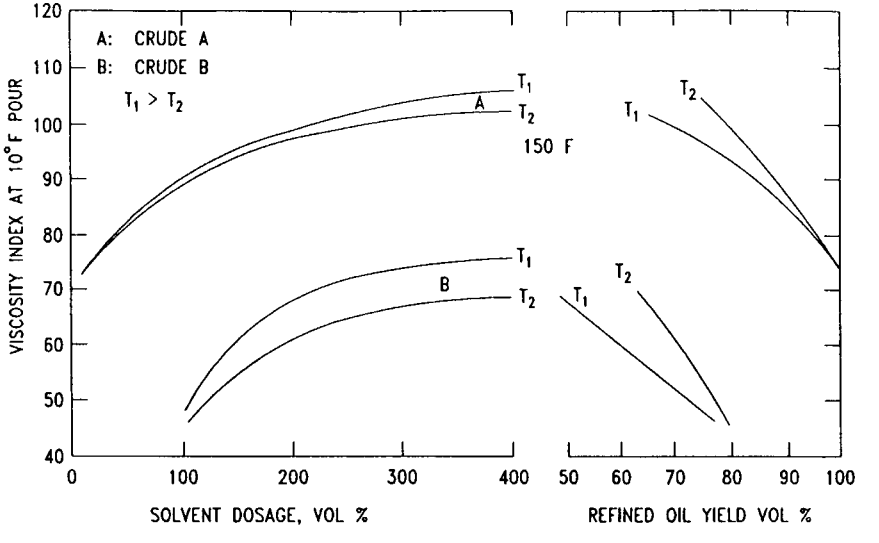


Figure 5.18 Solvent extraction of light neutral distillates—effect of crude source. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

Table 5.14 Refining Response of U.S. Mid-continent Distillates

	100 Neutral Distillates					
	Furfural		MP		Phenol	
Solvent Mid-continent crude	-B-	-C-	-B-	-C-	-B-	-C-
Dosage, vol %	260	210	155	140	220	165
Raffinate yield, vol %	73	66	74	64	64	65
Dewaxed oil visc. index	91	93	91	93	91	93
Dewaxed oil pour point, °F	10	10	10	10	10	10
	150 Neutral Distillates					
	Furfural		MP		Phenol	
Solvent Mid-continent crude	-A-	-B-	-A-	-B-	-A-	-B-
Dosage, vol %	105	215	65	145	125	210
Raffinate yield, vol %	90	74	90	76	87	71
Dewaxed oil visc. index	105	95	105	95	105	95
Dewaxed oil pour point, °F	0	5	0	5	0	5
	500 Neutral Distillates					
	Furfural		MP		Phenol	
Solvent Mid-continent crude	-A-	-B-	-A-	-B-	-A-	-B-
Dosage, vol %	300	260	180	135	300	195
Raffinate yield, vol %	65	70	68	68	62	67
Dewaxed oil visc. index	93	88	93	88	93	88
Dewaxed oil pour point, °F	10	10	10	10	10	10

Reprinted from Ref. [9] by courtesy of Texaco, Inc.

D. Effects of Impurities [9]

Extract oil in the recycle solvent will result in an increase in the solvent dosage required to produce a given VI base oil as is depicted in Figures 5.19 and 5.20. The data reported in Figures 5.19 and 5.20 were calculated and are in good agreement with laboratory studies on the effect of extract in recycled MP and furfural.

The data presented in Figure 5.21 are from a study in which neat solvent and a solvent from an FRU containing light oil were used to extract a 130 neutral distillate. These data show that a considerable increase in solvent dosage is required when measures are not taken to minimize light oil carry over or when

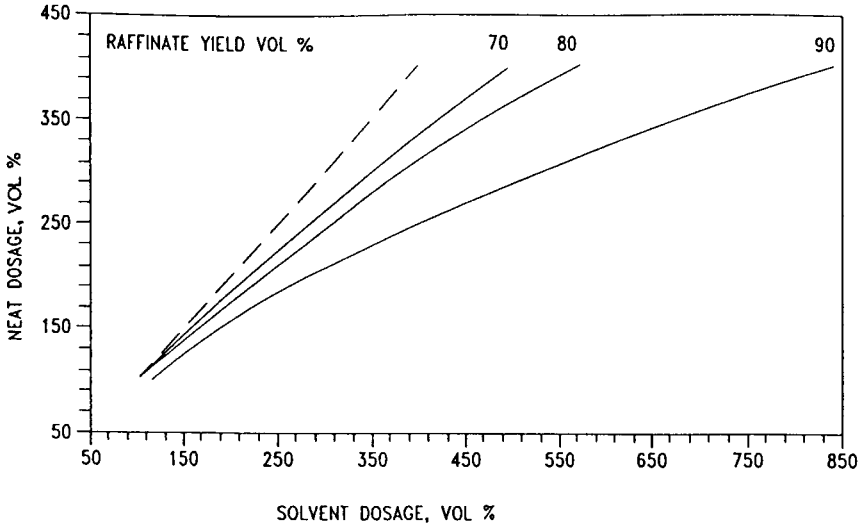


Figure 5.19 Effect of 1.5 vol percent extract on solvent dosage at different raffinate yields. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

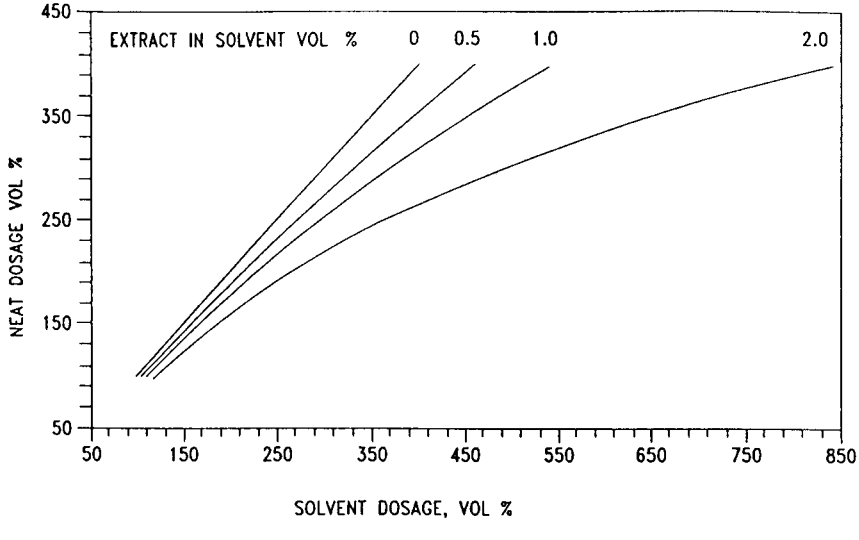


Figure 5.20 Effect of extract oil on solvent dosage at 85 vol percent raffinate yield. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

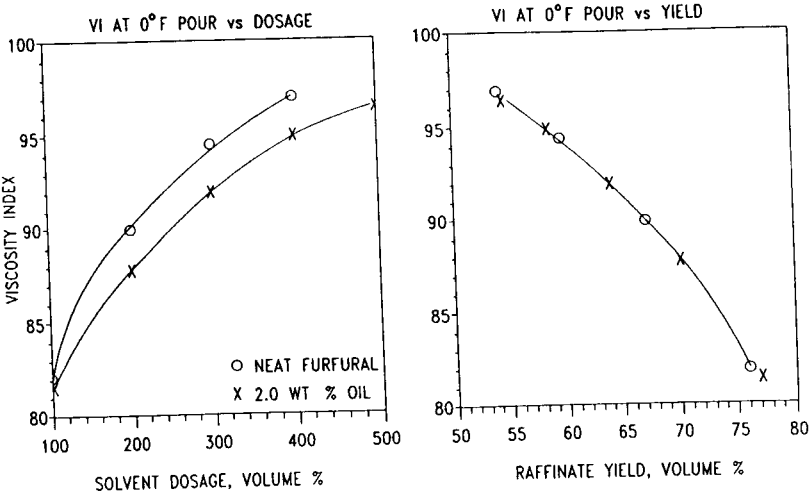


Figure 5.21 Effect of oil in solvent on refining response of 130 neutral distillate. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

units are operated above their design rates. The data also show that at a given VI level the raffinate yield was not affected by the oil present in the solvent.

It is also interesting to note that extract in the recycle solvent has a detrimental effect on the process whereas recycle of extract to the bottom of the extractor will not significantly affect the solvent dosage; in some cases extract recycle has proved beneficial as regards raffinate yield at a given VI with some feedstocks or when using stage-limited extraction devices.

Although it is desirable to minimize the water content of the recycle solvent, it should be noted that the use of water as a solvent modifier can be beneficial when extracting some feedstocks. However, water content of the recycle solvent will have a detrimental effect on the refining response of many lube feedstocks; solvent dosages and energy costs are higher when using solvent containing water.

E. Extract Recycle and Temperature Gradients [9]

Process studies have shown that the use of large temperature gradients and extract recycle are not cost-effective methods of increasing refined oil yield. Although improvements in yield and dosage may be obtained with some feedstocks, the data generally show that the results are within test repeatability if a properly designed extractor is used.

IV. EXTRACTION DEVICES [2,5,23]

Several types of extraction devices which are used in the major lube extraction processes are listed In Table 5.15

Packed towers and baffle trayed towers are the most widely used contactors for phenol refining whereas packed towers and RDCs have been the most widely used for furfural refining. Although all of the above contactors have been used with MP, the most widely used contactors appear to be packed towers and baffle tray towers because the major use of MP to date has been in converted phenol refining units.

Figures 5.22, 5.23 and 5.25 to 5.28 present simplified sketches of a few types of extraction devices used for the extraction of lube base stocks. It should be noted that these extractors must handle several different feedstocks of different viscosity and density from a variety of crudes in blocked operation. The need to process these feeds at a variety of operating conditions makes design of these units more critical than for those extractors used for many petrochemical extractions. Design information for lubricant base oil extractors are proprietary and extractor designs are usually provided under license by the refining process licensor or by equipment manufacturers. Engineering and construction contractors will in some cases design and construct the extractors.

The most widely used extraction device is probably the packed tower. The number of beds and types of packing used vary widely and probably include all of the known packing materials.

The major advantage for use of the RDC, Figure 5.23 [23], is that a wide range of throughputs can be handled by varying the rotor speed and there is a low holdup of solvent and oil as compared to packed towers and baffle towers. RDCs usually have a coalescer in the settling section and the interface between the solvent-rich and oil-rich phases is located near the top as compared to the bottom as is done in some packed towers. The RDC is now used in both fur-

Table 5.15 Lube Extractors in Use

Extractor type	Solvent
Packed towers	Furfural, MP, phenol
Rotating disc contactors	Furfural, MP
Baffle trayed towers	MP, phenol
Centrifugal contactors	Furfural, MP, phenol
Schiebel columns (Lab only)	Furfural, MP, phenol
Mixer-settlers (Lab only)	Furfural, MP, phenol

Reprinted from Ref. [9] by courtesy of Texaco, Inc.

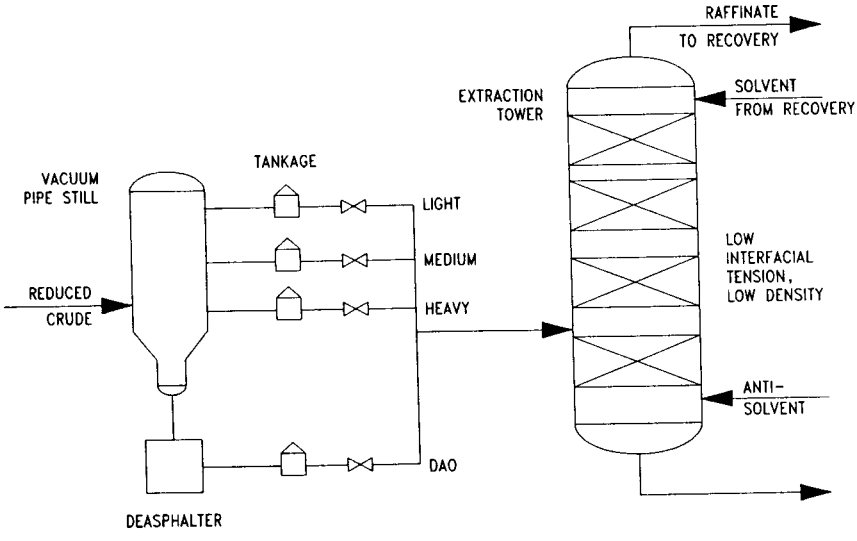


Figure 5.22 Blocked operation of packed extraction tower. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

fural and MP refining units as well as in deasphalting service. Although this is a preferred extractor for furfural refining, it should be noted that it does use rotating parts which can be a maintenance problem. Fortunately the rotor can be shut off (becoming a disc and donut tower) if the unit is operated at high throughputs. Capacity curves for the furfural refining of lubricant base oil feedstocks as reported by Reman [23] are presented in Figure 5.24; the terms are defined below.

$$\text{Specific energy input} = E = N^3R^5/HD^2$$

$$\text{Total specific load} = T = \text{Oil + furfural in gal/sq.ft./hr.}$$

Where D = Tower diameter in feet
H = Height of a compartment in feet
N = Rotor speed in revolutions per second
R = Diameter of the rotor in feet

Trayed towers are used in phenol and MP refining and provide excellent performance if designed properly. Since phenol and MP require less mixing and more coalescence time than does furfural, the baffle towers and packed towers have been widely used for this service. Examples of some of the trayed towers in use are presented in Figures 5.25, 5.26 and 5.27. Design information concerning these extractors is proprietary to licensors of the processes.

Centrifugal contactors as depicted in Figure 5.28 have been used in furfural and phenol refining of lube oils.

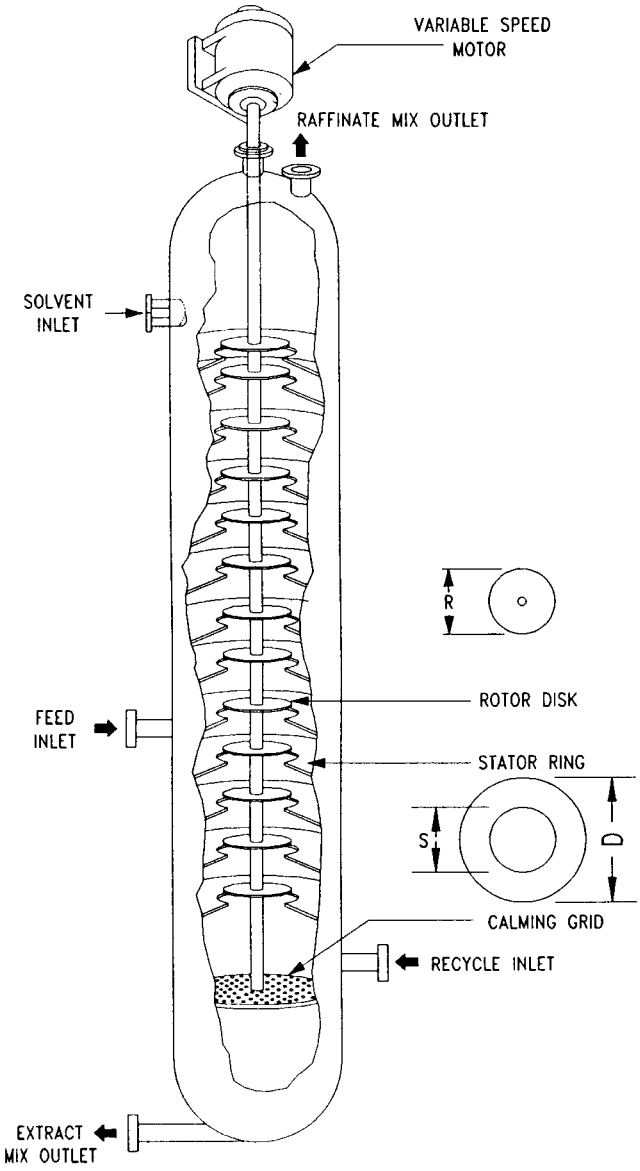


Figure 5.23 Rotating disc contactor.

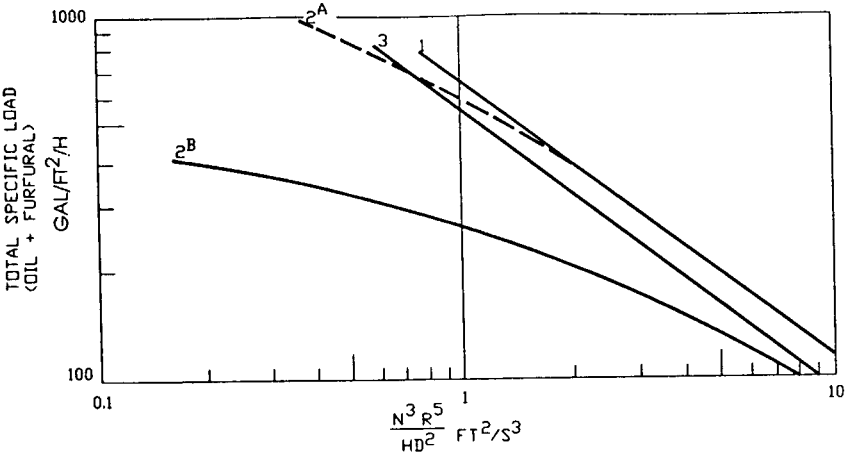


Figure 5.24 Flooding curves for various feedstocks with furfural. 1, Light and medium distillates—solvent ratio 2. O; 2, Heavy distillates—solvent ratio 3.0 (A = no emulsification, B = strong emulsification); 3, Deasphalted oils - solvent ratio 3.4.) (Reprinted from *Petroleum Refiner*, September, 1955, Gulf Publishing Co.)

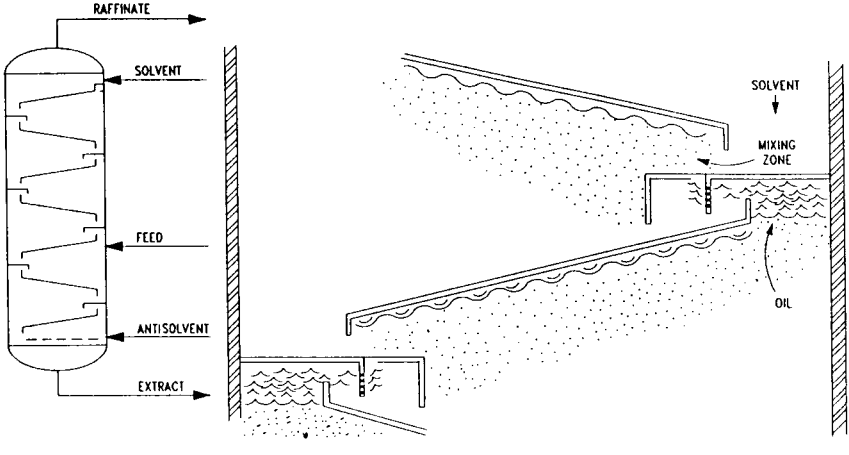


Figure 5.25 Segmented baffle trayed extraction tower. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

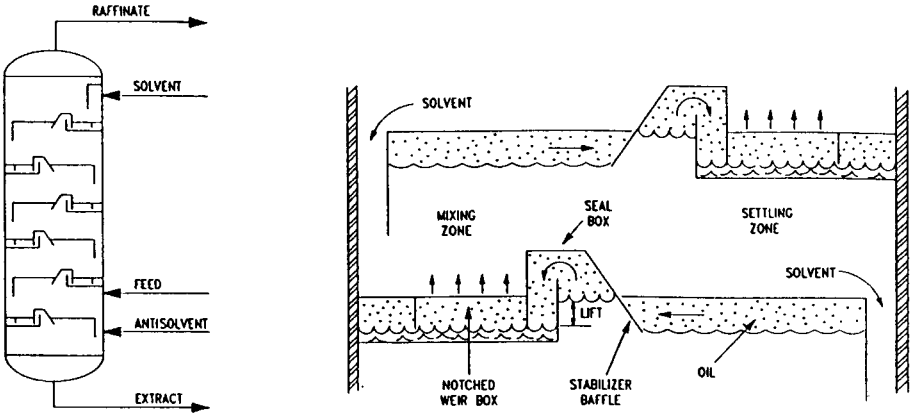


Figure 5.26 Underflow weir trayed tower. (Reprinted from Ref. [12], p. 160, by courtesy of Exxon Research and Engineering Co.)

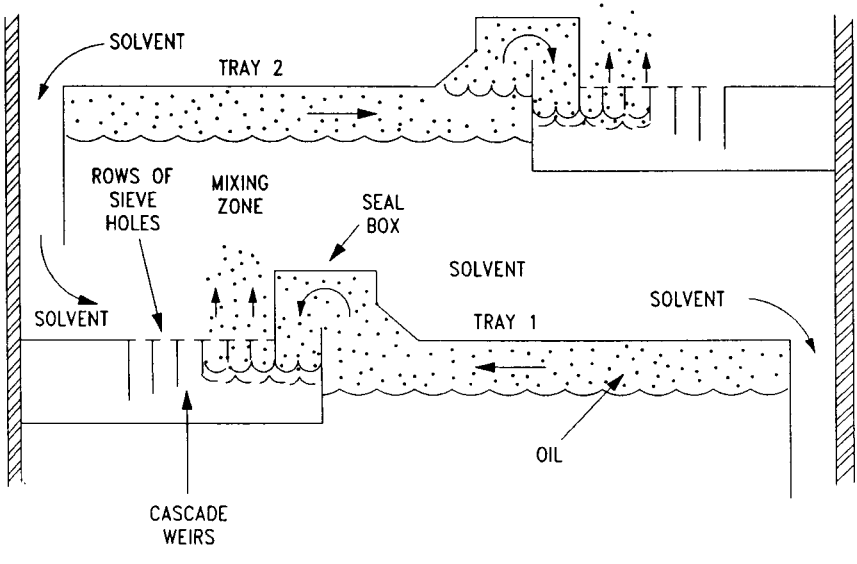


Figure 5.27 Cascade weir trayed tower. (Reprinted from Ref. [12], p. 161, by courtesy of Exxon Research and Engineering Co.)

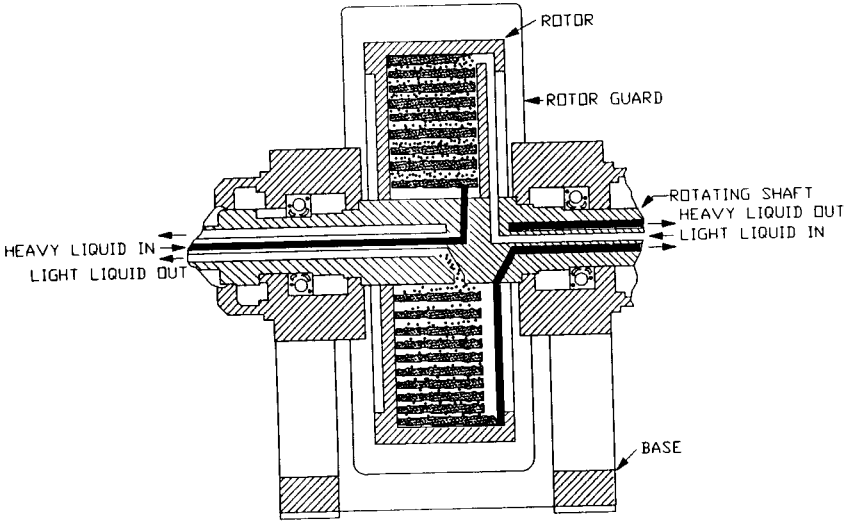


Figure 5.28 Centrifugal contactor. (Reprinted from Ref. [8], p. 382, by courtesy of McGraw-Hill Book Co.)

V. CONVERSION OF FURFURAL AND PHENOL UNITS TO MP

Refiners have in recent years converted furfural and phenol refining units to the use of MP. More phenol than furfural units have been converted because of the toxicological nature of phenol. These refiners have also found that solvent dosages have been lower with MP and that yield has been improved in some cases. Those interested are referred to references [12,13,14,15,17,20,21].

The reasons for conversion to MP are summarized below.

Significant increase in refining capacity
Significant reduction in energy costs
Use of marginal quality crudes
Reduced maintenance costs
Reduced solvent toxicity
Reduced solvent losses

A summary of the items which must be checked to determine the changes which should be made to permit conversion of a furfural or phenol refining unit to MP is provided in Table 5.16 [20].

Table 5.16 Checklist for Conversion to MP

Vapor velocities in vapor lines and exchangers
Vapor velocities in the extract heater
Metallurgy of the extract circuit
Extractor, flash tower and stripper capacities
Neutralization and inert gas blanketing systems
Capacities of the raffinate recovery section
Capacities of the extract recovery section

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The modifications required will depend on the results of the study and are dependent on the specific design of each individual unit and proposed throughput. A summary of the probable changes are shown in Table 5.17.

A simplified flow diagram for a phenol-refining unit after conversion to MP refining is shown in Figure 5.29. A comparison of this flow diagram with that of the phenol unit shown in Figure 5.9 shows that only minor modifications of the unit flow and raffinate recovery section were required to permit increasing capacity from 2500 to 3500 BPOD.

Results for operation of the unit are summarized in Table 5.18 [14]. It should be noted that this was a minimum-cost conversion and no effort was made to reduce energy consumption of the 1950s phenol design: that is, no steps were taken to recover and reuse energy as is done on new designs.

Conversion of a furfural refining unit to MP results in a unit which looks much like a Texaco Furfural Refining Unit; see Figures 5.5 and 5.6. The flow changes of these units are basically a change in the solvent purification system. In some designs the solvent drying system is changed as shown in Figure 5.30; in other cases the A–B fractionators are replaced with one new drying tower in which the flow becomes that of Figure 5.6.

Costs for conversion of a furfural refining unit to the use of MP are summarized in Table 5.19. These data are based on updates of previously reported

Table 5.17 Modifications for Conversion to MP Refining

Type of unit	Furfural	Phenol
Change in metallurgy	Limited	Limited
Flow distribution	Minor	Minor
Inert gas blanketing	Exists	Added
Solvent purification	Minor	Minor
Neutralization	Minor	Added

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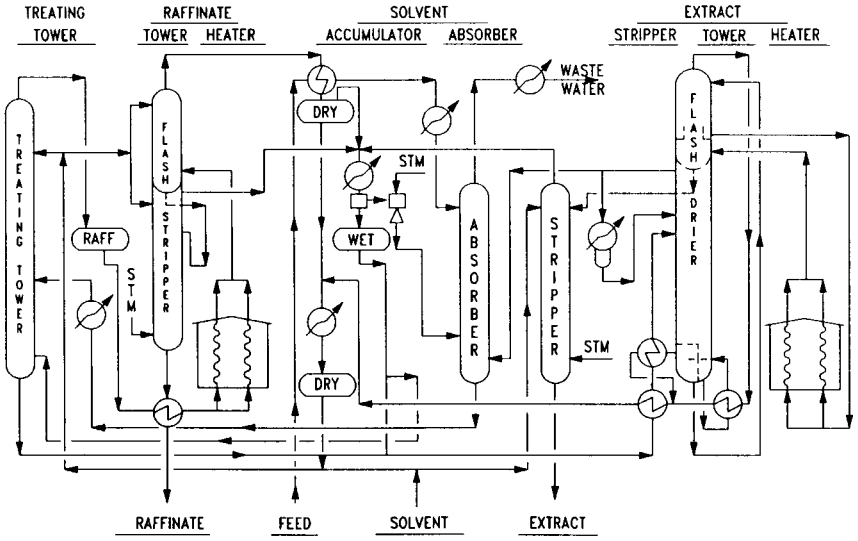

Figure 5.29 MP refining unit—converted phenol refining unit. (Reprinted from Ref. [14] by courtesy of Texaco, Inc.)

Table 5.18 Conversion of a Phenol Unit to MP Refining

Feedstock		North LA 150 neutral	
Conversion cost, 1978 $		400,000[a]	
Solvent inventory, $		260,000[b]	
Solvent	Phenol	MP	Change %
Design capacity, BPOD	1740	3540	+103
Demonstrated, BPOD	2500	4000+	+60
Refined oil yield, vol %	81.5	85.0	+4.3
Utilities per barrel of feed	[c]	[d]	
Cooling water, gals	792	447	−44
125 psig steam, pounds	36.5	8.5	−77
Fuel gas, MCF	220	229	+4
Electricity, kWh	1.6	1.0	−37

[a] Includes cost of slop and solvent tankage.
[b] Includes 25% safety factor for losses and startup.
[c] Reported consumption at 2500 BPOD on different crude.
[d] Reported consumption at 3540 BPOD.
Reprinted from Ref. [14] by courtesy of Texaco, Inc.

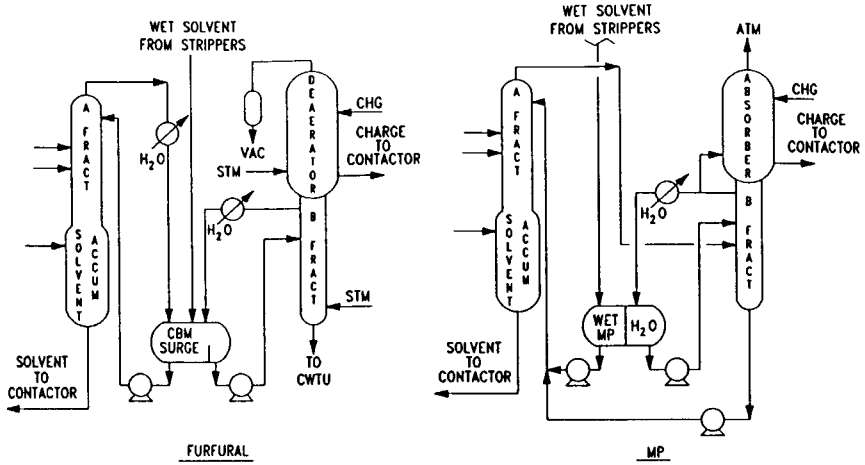

Figure 5.30 Wet solvent recovery section: furfural versus MP. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

cost information [2,16]. Energy reductions of about 20 to 30 percent and capacity increases of 20 to 30 percent are usually realized on conversion of furfural refining units to the use of MP.

VI. ENERGY REDUCTION TECHNIQUES [2]

A. Multiple Effect Evaporation

The solvent based processes used for the manufacture of lube oils are energy intensive because large volumes of solvent must be recovered by flash distilla-

Table 5.19 Conversion of a Furfural Unit to MP Refining [2,16]

	Mid-continent feedstocks		
Conversion cost, 1992 $	1,900,000–2,800,000		
Solvent inventory, $	560,000		
Solvent	Furfural	MP	Change %
Feedstock rate, BPOD	6,000	9,000	+50
Utilities per barrel of feed			
150 psig steam, lbs	0.42	0.0	−100
40 psig steam, lbs	10.3	5.0	−51.5
Fuel gas, MCF	140	118	−15.7
Electricity, kWh	0.95	0.73	−23.2

Reprinted from Ref. [2] and [16] by courtesy of Texaco, Inc.

tion for recycle in the process. The number of stages used for evaporation of the solvent has a significant effect on the energy costs for these processes and as many as five evaporation stages were used in some early liquid sulfur dioxide extraction units located in Europe. Since energy was cheap, most of the units built between about 1950 and 1975 used double-effect evaporation and a few refiners used single-effect evaporation. Because the cost of energy increased rapidly during the 1970s, most new units built since about 1980 have been designed with (and older units converted to) triple-effect evaporation to reduce the cost of energy consumed in these processes. A comparison of the effect of the number of stages on multistage evaporation is summarized in Table 5.20. Simplified flow diagrams for the double-effect and triple-effect evaporation schemes are provided in Figures 5.31 and 5.32.

B. Inert Gas Stripping

Inert gas stripping is another method which can be used to reduce energy requirements in solvent refining units [2,12]. It should be noted that inert gas stripping was used by Exxon in phenol refining in the late 60s and is used in some EXOL N refining units; see Figure 5.8. A simplified flow diagram for an inert gas stripping section in a solvent-based process is depicted in Figure 5.33 [2].

C. Integration of Process Units

Reductions in energy costs and capital costs from reduced tankage and inventory can be realized from integrating process units [2,24]. The integration of

Table 5.20 Comparison of Evaporation Stages

Single-effect
1. Solvent is vaporized at one pressure level.
2. Energy is wasted in condensation; it is not recovered.

Double-effect
1. Solvent is vaporized at two pressure levels.
2. One-half of the solvent is vaporized at each pressure level.
3. Condensing vapors are used to operate the first evaporator.
4. Energy requirements are reduced by 45 to 50 percent.

Triple-effect
1. Solvent is vaporized at three pressure levels.
2. One-third of the solvent is removed at each pressure level.
3. Condensing vapors are used to operate the first two stages.
4. Energy requirements are reduced by an additional 30–33 percent compared to double-effect evaporation.
5. Energy requirements are 30 to 33 percent of single-effect.

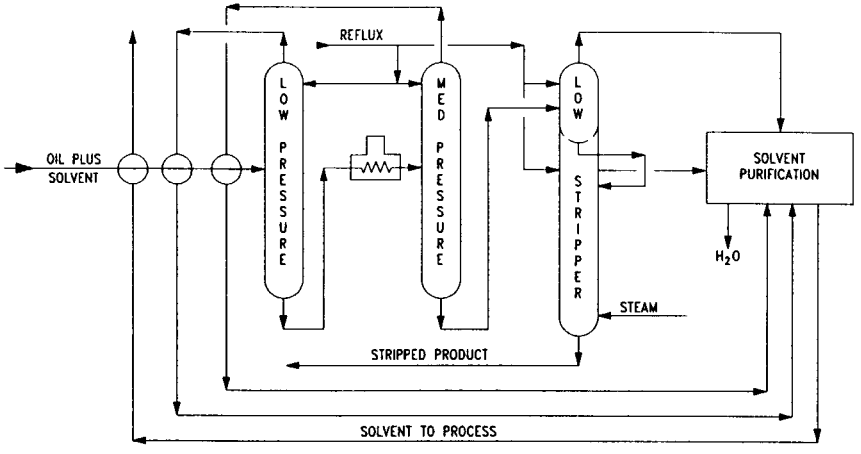

Figure 5.31 Dual effect evaporation. (Reprinted from Ref. [2] by courtesy of Texaco, Inc.)

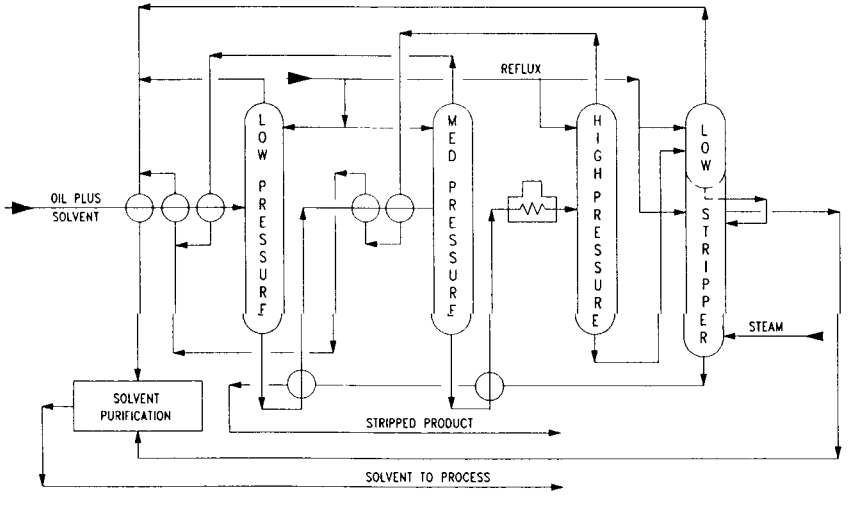

Figure 5.32 Triple effect evaporation. (Reprinted from Ref. [2] by courtesy of Texaco, Inc.)

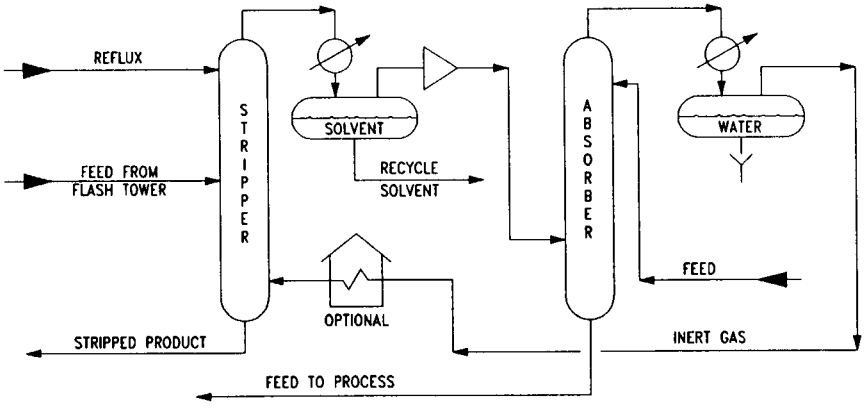

Figure 5.33 Inert gas stripping and feed dehydration. (Reprinted from Ref. [2] by courtesy of Texaco, Inc.)

deasphalting units with propane dewaxing units, crude units with hydrocrackers and solvent refining units with hydrogen-finishing units are obvious integrations practiced by a few lube refiners. However, most refiners do not integrate units to avoid lost production resulting from complete loss of production when any unit shutdown occurs; the many grades of base oils manufactured may result in duplicate process units and the extra manpower and complications resulting from undergoing test and inspection on multiple units at the same time.

D. Other Energy-Reducing Techniques

Although steam generation using base oil processing units is practiced, it is not widely used by base oil refiners. The patent literature indicates that refiners are evaluating membrane separation techniques for the recovery of solvent. However, it does not appear that this technique is being used on a commercial scale.

Other energy reducing techniques which could be used include the addition of additional evaporation stages and the use of vapor recompression. The use of more than three stages of evaporation is not now practiced and no known base oil manufacturing operations using vapor recompression have been identified.

VII. INVESTMENT AND UTILITY REQUIREMENTS

Investment and utility requirements are site-specific and vary widely depending on unit feed capacity, solvent-to-feed ratio, feedstock quality, product quality and product slate. The degree of process integration and degree of energy-

reduction techniques used will also affect the investment and utility requirements. Accurate investment and operating costs can therefore only be determined by a detailed design and definitive estimate for the particular feedstocks and products to be manufactured. Investment and utility requirements for various solvent refining processes are available from licensors with some information being published on a biannual basis in *Hydrocarbon Processing*. Some investment and utility requirements are provided in Table 5.5, 5.18 and 5.19.

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6

Lubricant Base Oil Hydrogen Refining Processes

I. INTRODUCTION

In lube processing, the emphasis is on the removal of undesirable components such as aromatics and other low VI materials by solvent extraction. Hydrogen refining is becoming of greater importance today because it converts the undesirable constituents into the desirable lubricant base oil components and other higher valued by-products.

Hydrogen refining, commonly called lube hydrocracking or severe hydrotreating was first used in the 1930s and discontinued because the then co-emerging solvent refining processes were more cost-effective [1,2]. A cheap source of hydrogen resulting from the use of catalytic reforming units and the need by some refiners to use less desirable crudes for base oil manufacture led to reintroduction of the hydrogen refining processes in the early 1970s [3,4,5,6].

The hydrogen refining processes are more severe than the mild hydrogen finishing processes used as a replacement for the older chemical finishing processes. The hydrogen finishing processes are discussed in Chapter 9 on finishing. The hydrogen refining processes consist of (1) the severe hydrotreating (lube hydrocracking) processes and (2) the speciality oil hydrogenation (hydrorefining) processes.

The types of chemical reactions which occur in the hydrotreating processes are listed below and depicted in Figure 6.1 [6].

HYDROGEN FINISHING – PURIFICATION REACTIONS

HYDROREFINING – PURIFICATION AND SATURATION REACTIONS

HYDROCRACKING – PURIFICATION, SATURATION AND CRACKING REACTIONS

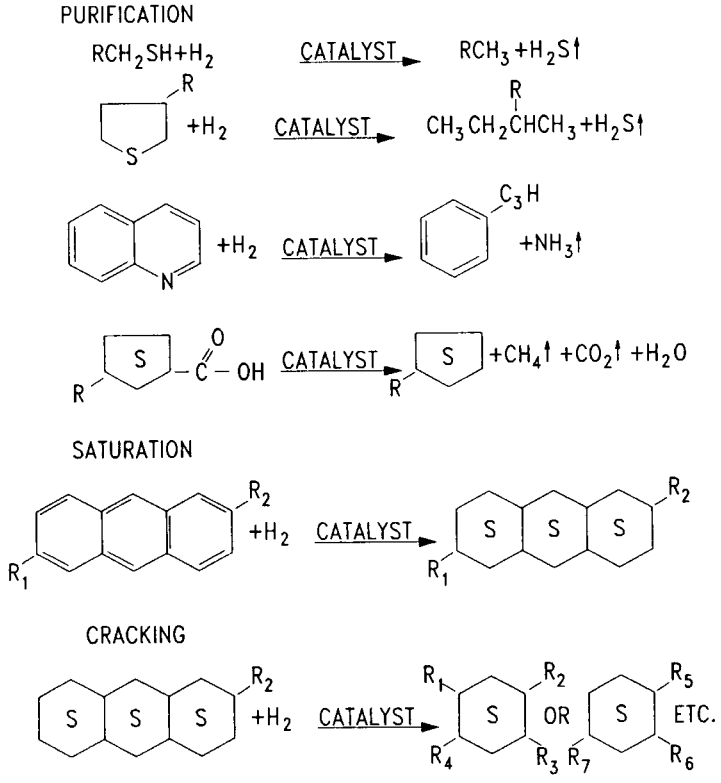

Figure 6.1 Chemical reactions of hydrotreating processes. (Reprinted from Ref. [6], p. 900 by courtesy of Chevron International Oil Co.)

A. Purification Reactions

These reactions normally involve low to moderate severity catalytic hydrogenation to remove trace quantities of sulfur, nitrogen, and oxygen. There is no marked change in the composition or molecular distribution of the hydrocarbons unless contaminant concentration is high. Operating conditions are on the order of 200 to 2000 psi hydrogen partial pressure, 500 to 700°F catalyst temperature and 1 to 5 space velocity. Although chemical hydrogen consumption

is usually on the order of 100 standard cubic feet per barrel, it may be a few hundred standard cubic feet per barrel for some feedstocks with large quantities of sulfur-, nitrogen- and oxygen- containing compounds.

B. Saturation Reactions

These reactions involve the purification reactions and saturation reactions that convert olefins to paraffins and aromatics to cycloparaffins. Product molecular weight distribution is not markedly different from the feed unless the feed has appreciable quantities of sulfur, nitrogen, oxygen and polynuclear aromatics. Operating conditions are on the order of 500 to 3000 psi, 450 to 750°F temperature and 0.5 to 3.0 space velocity. Chemical hydrogen consumption ranges from about 100 to 1000 standard cubic feet per barrel of feedstock.

C. Cracking Reactions

These reactions involve the breaking of carbon-to-carbon bonds, scission of condensed ring structures and molecular rearrangement via isomerization. Hetero atoms are removed almost completely and saturation reactions also occur. Although operating pressures range from 500 to 4500 psi, pressures of 2000 to 3000 psi are most often used. Temperatures range from 625 to 850°F and space velocities range from 0.5 to 3.0. Chemical hydrogen consumption is on the order of 500 to 2000 standard cubic feet per barrel depending on the feedstock composition and operating conditions.

The purification reactions are representative of those reactions which occur in the mild hydrotreating or hydrogen finishing processes. The purification and saturation reactions are representative of the reactions which occur in the moderate severity hydrotreating or hydrorefining processes. All of the reactions (purification, saturation and cracking) are representative of the reactions which occur in the hydrocracking processes.

The hydrocracking processes and hydrorefining processes will be discussed in this chapter and the hydrogen finishing processes will be discussed in Chapter 9.

II. HYDROCRACKING PROCESSES

The lube hydrocracking processes are the most severe lubricant base oil hydrogen refining processes and are most often used (1) to permit use of low quality crude oils, (2) for viscosity reduction, (3) as a replacement for solvent extraction and (4) to improve the quality of lubricant base oils or (5) to increase the yield of base oils obtained by solvent extraction [5,7,8,9,10,11,12,13,14,15].

A. Process Flow

A simplified flow diagram for a lubricants base oil hydrocracking unit is shown in Figure 6.2 [16]. The feedstock is heated to the reaction temperature, mixed

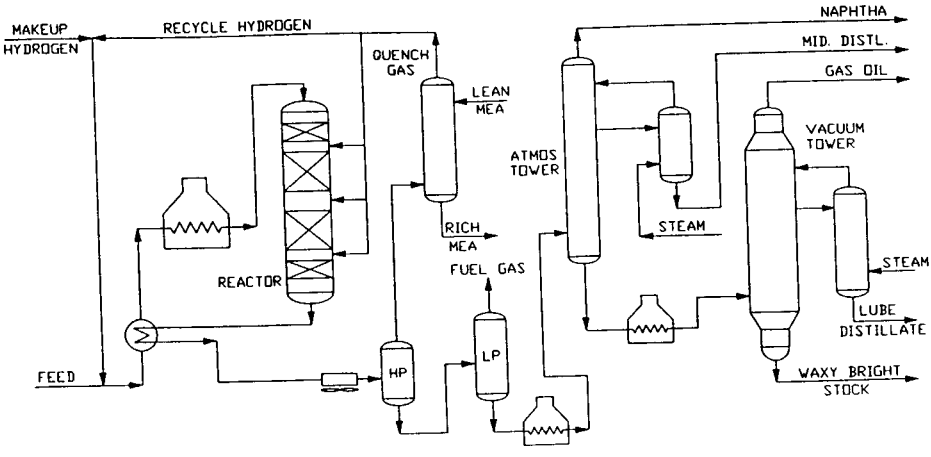

Figure 6.2 Bulk feed hydrocracker flow diagram. (Reprinted from Ref. [6], p. 359.)

with hydrogen and passed downflow over a series of catalyst beds or through a series of reactors. Hydrogen quench is used between the beds of catalyst to remove the heat generated by the exothermic reactions and control the reaction temperature. The effluent from the reactor passes through a series of separators to remove the hydrogen and light hydrocarbons. The effluent product is then fractionated in atmospheric and vacuum distillation towers to provide the desired lube stocks and by-products. The effluent gas (mostly hydrogen) from the process is purified and recycled in the process. The fractionated base oil fractions are then dewaxed or dewaxed and hydrorefined to prepare a finished base oil. Some refiners solvent extract the feed to the hydrocracker or solvent extract the hydrocracked base oils before or after dewaxing.

B. Effect of Hydrocracking on Feedstock Properties

Hydrocracking markedly reduces the viscosity of the feedstock; removes most of the nitrogen, oxygen and sulfur present in base oil feedstocks and converts the undesirable low VI materials such as polynuclear aromatics and polynuclear naphthenes to higher VI materials such as mononuclear naphthenes, mononuclear aromatics and isoparaffins. A summary of the effects of hydrocracking on the properties of the feedstock are summarized in Table 6.1. The viscosity index of the different types of compounds found in hydrocracked base oils is provided in Table 2.13.

C. Feedstocks to Hydrocracking Processes

The feedstocks to the hydrocracking processes are listed in Table 6.2.

Table 6.1 Effects of Hydrocracking on Properties of Base Oil Feedstocks

Decreases viscosity	Increases viscosity index
Improves color	Reduces color stability
Improves inhibitor response	Decreases oxidative stability
Reduces sulfur content	Reduces nitrogen content
Reduces carbon residue	Reduces specific gravity
Reduces aromatic content	Increases iso-paraffin content
Increase naphthene content	Permits use of non-lube crudes

D. Comparison with Solvent Extraction

Hydrocracking offers some advantages over solvent refining; the major advantages being manufacture of higher VI base oils and the manufacture of base oils from low quality crudes. A comparison of the hydrocracking process with the solvent extraction processes is presented in Table 6.3.

E. Processing Conditions [7,9,13,14,15,16,17,18]

The operating conditions of the lube hydrocracking processes are dependent on the composition of the feedstocks and catalyst used as well as on end use of the base oils produced. The range of operating conditions are presented in Table 6.4 [16].

The higher pressure (4000+ psig) units currently being used in some eastern European countries are coal hydrogenation units which were converted to vacuum gas oil and deasphalted oil hydrocrackers.

F. Hydrocracking Catalysts

The catalyst being used in the lube hydrocracking processes are generally proprietary to the licensors of the processes and consist of cobalt–molybdenum on alumina, nickel–molybdenum on alumina, nickel–tungsten on alumina, and nickel–tungsten on silica alumina. The nickel–tungsten on alumina appear to be the most widely used catalysts with some refiners using fluoride injection to enhance catalytic activity.

Table 6.2 Feedstocks to Lube Hydrocracking

Unrefined distillates	Solvent refined distillates
Deasphalted oils	Solvent extracted deasphalted oils
Hydrocracked deasphalted oils	Scale and slack waxes
Mixtures of the above	

Table 6.3 Comparison of Hydrocracking and Solvent Refining

Advantages of hydrocracking
Higher VI base oils
Higher yields of base oils
Higher valued by-products
Use of poorer quality crudes
Viscosity adjustment to meet demand
Base oils of better inhibitor response
Elimination of finishing in some cases
Conversion of residual oils to distillate oils
Disadvantages of hydrocracking
Form sludge and darken on exposure to heat or light
Require stabilization by extraction or hydrorefining
Investment costs are higher at the 95 VI level
Operating costs are higher at the 95 VI level
Solvent dewaxing filter rates are poorer
Catalytic dewaxed bright stocks are hazy
Uninhibited base oil oxidation is poorer
Exhibit additive solubility problems
Aromatic extract oils are not produced

Although the catalysts listed in Table 6.5 are examples of catalysts which can be used to prepare lubricant feedstocks, a more complete listing can be found in the *Oil & Gas Journal* [19,20]. The catalysts listed in Table 6.5 [19,20] are not all-inclusive, because many of the catalysts used in the other hydrotreating processes may also be used for lube hydrocracking.

Table 6.4 Lube Hydrocracking Process Conditions

Process variable	Operating conditions	
	Range	Typical
Pressure, psig	1500–4000+	2500–3000
Temperature, °F	625–850	725–825
Space velocity, Vo/Vc/hr	0.25–1.25	0.5–1.0
Hydrogen recycle, SCFB	3000–8000	3500–5000
Recycle hydrogen purity, mole %	70–100	90–95
Hydrogen consumed, SCFB	500–3000	700–1200
Lube yield, volume %	30–90	40–80
Catalyst life, years	1–3	1–2

Reprinted from Ref. [16], p. 356.

Table 6.5 Some Commercially Available Hydrocracking Catalysts

Supplier	Name	Composition		License required
		Metals	Support	
Akzo	KF-840	Nickel–molybdenum	Alumina	No
	KF-843	Nickel–molybdenum	Alumina	No
	KF8010	Nickel–molybdenum	Alumina	No
	KF-746	Cobalt–molybdenum	Alumina	No
Chevron	ICR-126	Proprietary	Proprietary	Yes
	ICR-113	Proprietary	Proprietary	Yes
	GC-30	Proprietary	Alumina	Yes
	GC-36	Proprietary	Alumina	Yes
Criterion	C-424	Nickel–molybdenum	Alumina	No
	C-354	Nickel–tungsten	Alumina	No
	C-454	Nickel–tungsten	Alumina	No
Engelhard	HPC-50	Nickel–molybdenum	Proprietary	No
	NI-4342	Nickel–tungsten	Alumina	No
	NI-4352	Nickel–tungsten	Alumina	No
Lyondell	ARCO H-H	Proprietary	Proprietary	Yes
United Catalysts	C20-7	Nickel–molybdenum	Alumina	No
Unocal/UOP	DHC-2	Proprietary	Amorphous	Yes
	DHC-8	Proprietary	Amorphous	Yes

Reprinted from Ref. [19] and [20] by courtesy of *Oil and Gas Journal.*

G. Hydrocracking Process Variables

The process variables for lube hydrocracking processes are listed in Table 6.6. Although operating pressure, hydrogen purity and hydrogen rate have a significant effect on catalyst life and product yield, other important variables are feedstock quality, temperature, space velocity and catalyst.

1. Effects of Feedstock Quality

The yield of lube base stock is highly dependent on the quality of the feedstock, base oil specifications, catalyst and process severity. Figure 6.3

Table 6.6 Lube Hydrocracking Process Variables

Feedstock	Pressure
Temperature	Space velocity
Catalyst	Hydrogen purity
Recycle hydrogen rate	

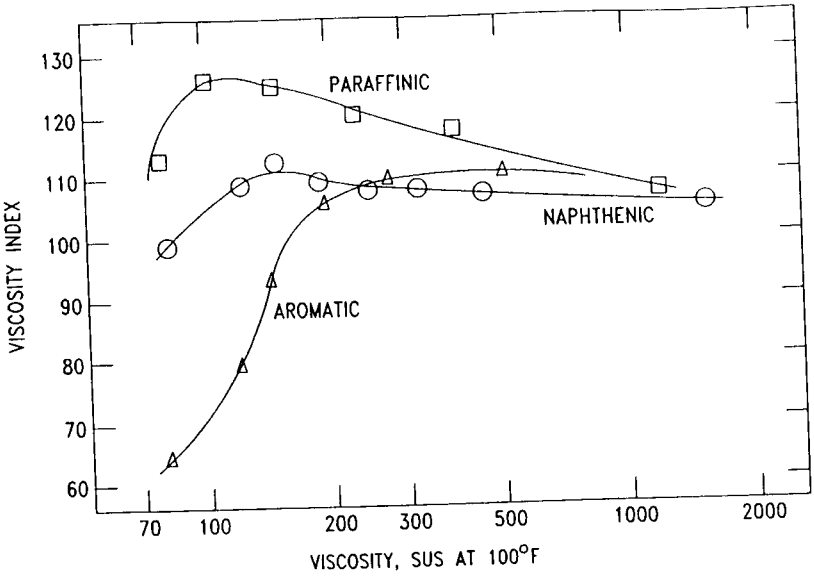

Figure 6.3 Effect of feed composition on product character. (Reprinted from Ref. [7], p. 451 by courtesy of M. Charles Bryson.)

presents the lube product quality (VI) which is obtained when hydrocracking a broad range mixture of distillate and deasphalted oil from different quality crudes [7,8]. The data show that the VI of the base stocks obtained from the hydrocracking of naphthenic crude feedstocks is nearly constant with viscosity. The VI of the base stocks from hydrocracking paraffinic crude feedstocks exhibits a somewhat higher VI for the low viscosity base stocks than for the higher viscosity base stocks. The base stocks from hydrocracked aromatic feedstocks are considerably lower for the low viscosity base stocks as compared to the higher viscosity base stocks [7,8]. Since the vast majority of feedstocks are more aromatic in nature, the behavior of the aromatic type feedstocks is most often observed when bulk feed hydrocracking is used.

The nature of the feedstock affects not only the VI but also the yield of the base stocks obtained. This is illustrated by the data presented in Tables 6.7 and 6.8 [7,8]. These data clearly show that the character of the feedstock affects both the viscosity index and yield of base oil.

2. Effects of Temperature and Space Velocity [7,8,9,21]

The process temperature and space velocity (LHSV) are the primary process variables which affect base oil VI and yield. The use of low space velocity is usually preferred over higher temperatures to reduce the amount of extraneous

Table 6.7 Effect of Feedstock Quality on Base Oil VI and Yield

Vacuum distillate	W. Texas	725–1025°F	No La.	800–1100°F
Base oil yield, volume %		42.0		44.2
Properties	Feed	Base oil	Feed	Base oil
API gravity	21.5	—	30.0	38.3
Viscosity SUS @ 210°F	60.1	43.3	58.5	39.5
Viscosity index	—	109	—	140
Pour point, °F	95	0	115	0
ASTM Color,	L 3.0 dil.	L 1.0	L 5.0 dil.	L 0.5
Sulfur, weight %	1.27	<0.03	0.25	<0.01
Carbon residue, weight %	0.84	<0.05	0.47	<0.05
Iodine number	19.0	5.3	9.1	4.3

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cracking and coke deposits on the catalyst. Figures 6.4 through 6.6 illustrate the effect of process severity on the quality and yield of the base oil [7,8,21].

These data show that an increase in process severity increases the viscosity index of the base oil. The data in Figures 6.5 and 6.6 also show that low space velocities provide a higher yield of the desired high VI components (iso-paraffins and mono-naphthenes) as compared to use of a higher space velocity and temperature [21]. Table 6.9 presents additional data on the effect of process severity on base oil quality [7, 8].

3. Bulk Feed Hydrocracking [7,12,14]

The use of bulk feed lube hydrocracking often leads to a low viscosity base oil fraction which is low in viscosity index in comparison to the heavy base oil fraction of the hydrocrackate. The difference in VI between the heavy and light base oil fraction is often called "VI droop". Data demonstrating this is provided in Table 6.10 which shows the properties of the feed and dewaxed bulk and fractionated base stocks obtained from Kuwait Deasphalted Oil.

Table 6.8 Effect of Feedstock Quality on Base Oil Yield

Crude source	U.S.A. blend	Lagomedia	Oficina
Feedstock dewaxed oil VI	75	60	43
Base oil yield, volume %	70	55	30
Dewaxed oil properties			
Viscosity index	100	100	100
Pour point, °F	0	0	0

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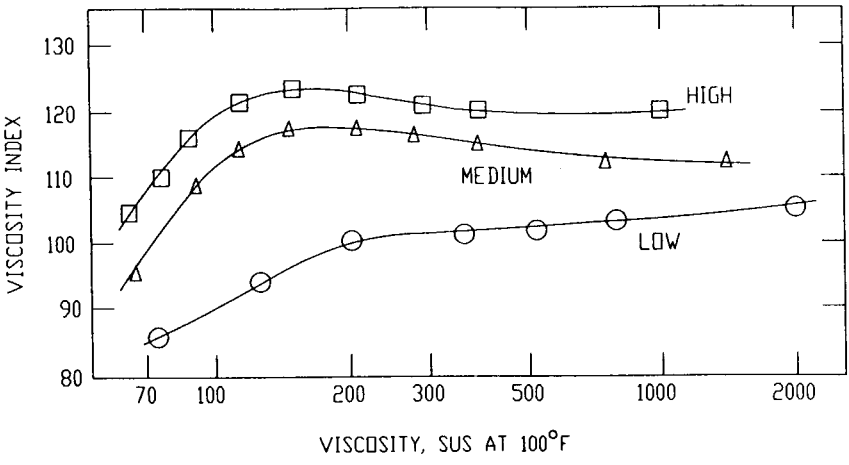

Figure 6.4 Effect of process severity on product character. (Reprinted from Ref. [7], p. 452 by courtesy of M. Charles Bryson.)

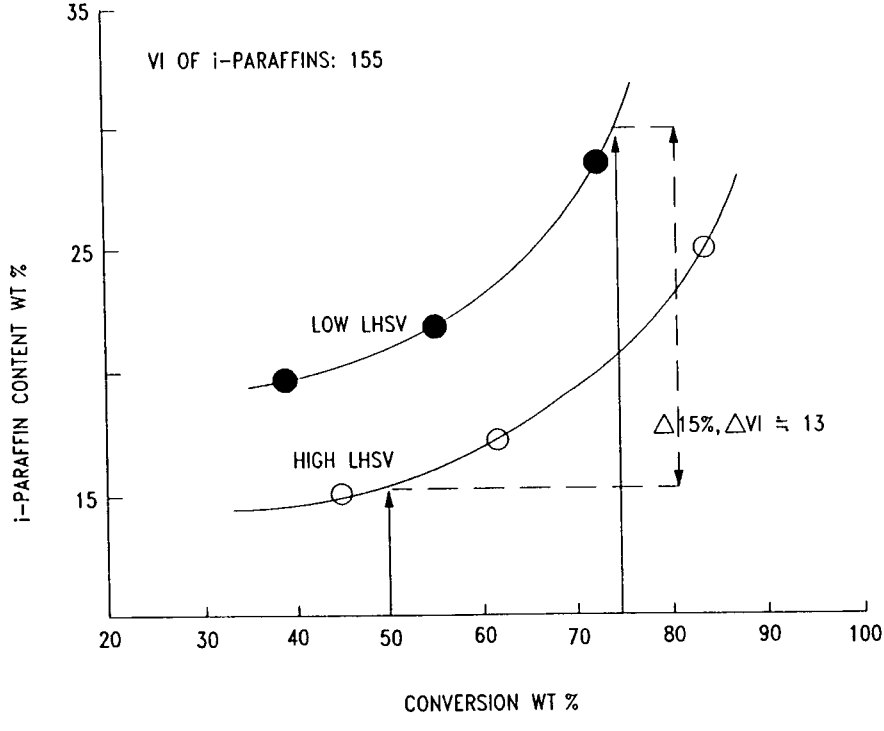

Figure 6.5 Effect of reaction conditions on iso-paraffin content. (Reprinted from Ref. [21], p. 1295 by courtesy of ACS and Nippon Oil Company, Ltd.)

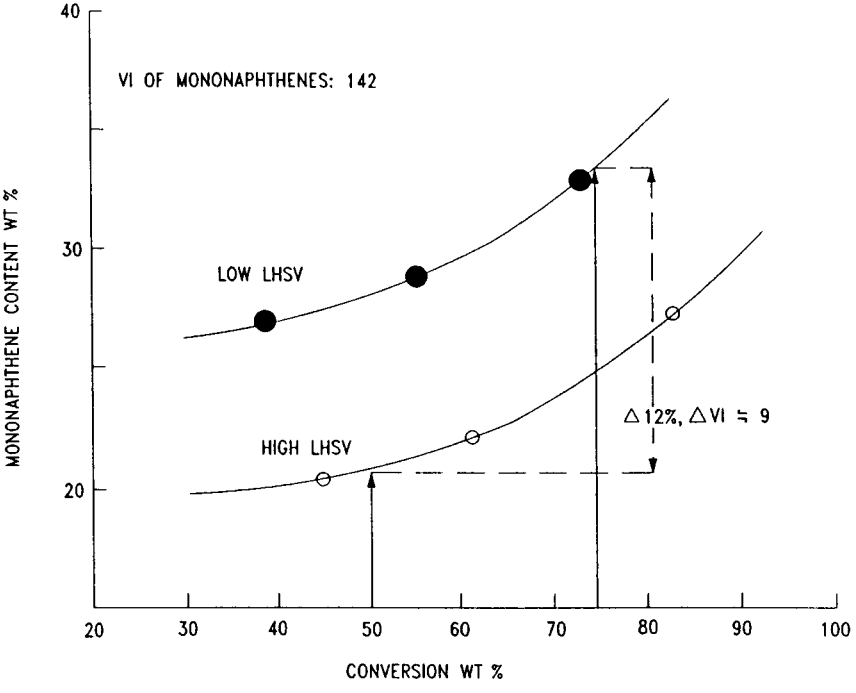

Figure 6.6 Effect of reaction conditions on mononaphthene content. (Reprinted from Ref. [21], p. 1295 by courtesy of ACS and Nippon Oil Company, Ltd.)

Table 6.9 Effect of Process Severity on Base Oil Yield and VI

	Feed	Low severity	High severity
Middle East	DA oil	Dewaxed oil	Dewaxed oil
Dewaxed oil yield, volume %		77.7	64.4
Base oil properties			
API gravity	19.8	24.9	28.6
Viscosity SUS @ 210°F	231	149.9	75.5
Viscosity index	74	84	103
Pour point, °F	130+	−10	−15

Reprinted from Ref. [8] by courtesy of M. Charles Bryson.

Table 6.10 Hydrocracking a Mixture of Distillate and DA Oil

	Feed	Product	Fractionated products		
Viscosity grade		500SN	150SN	500SN	BRTSTK
Dewaxed oil yield, wt %		66.5	18.6	33.3	14.6
Property					
Specific gravity	0.931	0.882	0.884	0.880	0.884
Viscosity cSt 100°C	20.50	11.71	5.20	11.10	32
Viscosity index	62	95	80	95	100
Pour point, °C	−21	−21	−21	−18	−18
Composition (ndm)					
Aromatics, wt %	21.4	5.0	6.5	3.9	3.3
Paraffins, wt %	51.9	67.0	58.8	67.0	69.8
Naphthenes, wt %	26.7	28.0	34.7	29.1	27.2

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A summary of the VI droop obtained when hydrocracking bulk feeds from Alaskan North Slope and Arabian Light crudes is presented in Table 6.11 [12]. These data show that the VI droop depends on crude source and is greater for poor quality as compared to good quality crude oils. Solvent extracted oils do not exhibit a VI droop; low- and high-viscosity fractions from a 95 VI neutral will have about the same VI as the parent base oil. Low- and high-viscosity fractions from unrefined feedstocks used to prepare base oils exhibit a decrease in viscosity index as the viscosity increases.

4. Blocked Feed Hydrocracking

Hydrocrackers are often operated in a blocked-out manner as shown in Figure 6.7 to overcome the VI droop for low viscosity base stocks [7,8]. VI droop can also be overcome by recycle of the light lube fraction in the bulk hydrocracking process [7,8].

Table 6.11 VI Droop in Lube Hydrocracking

	Alaskan North Slope		Arabian Light	
	Viscosity index	Droop	Viscosity index	Droop
500 neutral	100	Base	100	Base
240 neutral	92	8	99	1
100 neutral	75	25	88	12

Reprinted from Ref. [12], p. 49 by courtesy of *Oil & Gas Journal* and Chevron International Oil Company, Inc.

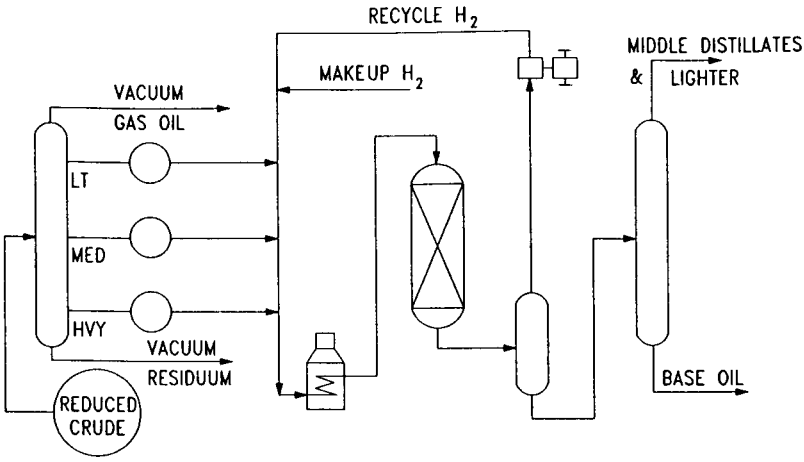

Figure 6.7 Blocked distillate lube hydrocracker flow diagram. (Reprinted from Ref. [7], p. 453 by courtesy of M. Charles Bryson.)

H. Stabilization of Hydrocracked Base Oils [7,8,10,18,24]

Hydrocracked oils tend to darken and form sediment on exposure to light. Methods used to stabilize these oils consist of clay treating, solvent refining or hydrorefining of the hydrocracked oil after dewaxing [7,10,18]. The effects of hydrorefining on the stability of a hydrocracked 500 neutral base oil are shown in Table 6.12 [8].

Minimal yield loss with retention of base oil properties was achieved with significant improvements in base oil stability properties. Yan [22] proposes alkylation of hydrocracked oils with olefins over acidic catalysts for stabilization and Bryers [10] and Asseff [24] report that hydrocracked oils can be stabilized with additives.

Figure 6.8 is a simplified flow diagram of Chevron's Richmond Lube Oil Plant (RLOP) based on the work of Farrel et al. [12,23]. This figure depicts two methods by which hydrocracking is incorporated in lubricant base oil production. The first method consists of hydrocracking followed by solvent dewaxing and high pressure hydrofinishing (hydrorefining) to stabilize the hydrocracked oils. The second mode of operation consists of hydrocracking followed by catalytic dewaxing and hydrorefining. The hydrorefining reactor is close-coupled with the catalytic dewaxing reactor and the effluent from the catalytic dewaxing reactor is the feed to the hydrorefining reactor.

I. Hydrocracking and Solvent Extraction Combinations

Figure 6.9 is a simplified flow diagram of Sun's Puerto Rican Lube Plant based on the work of Steinmetz [11]. In this plant, solvent extraction is used in con-

Table 6.12 Hydrorefining of a Hydrocracked 500 Neutral

	Before hydrorefining	After hydrorefining
API Gravity	27.4	29.4
Viscosity SUS @ 100°F	484	479
Viscosity index	95	97
Pour point, °F	0	0
ASTM color	L4.0	L0.5
Sulfur, weight %	0.09	0.008
Carbon residue, weight %	0.12	0.07
Total acid number, D 974	0.03	<0.03
Thermal stability		
12 hours at 170°C		
Appearance	Dark	Bright
Precipitate	Nil	Nil
ASTM color	8+	8.0
48 hours at 170°C		
Appearance	Dark	Bright
Precipitate	Medium	Nil
ASTM color	8+	8+
Ultraviolet light stability		
Hours to floc	70	340
ASTM color	3.5	2.5
Sunlight stability		
Days to floc	12	30+
ASTM color @ 30 days	4.5	L2.5

Reprinted from Ref. [8] by courtesy of M. Charles Bryson.

junction with hydrocracking for the manufacture of base oils. The heavy vacuum gas oil is furfural extracted to improve the VI and hydrocracking response of the heavy lube distillate. The heavy distillate is blended with the light distillate and hydrocracked using a bulk feed hydrocracker. The effluent from the hydrocracker is atmospherically distilled to remove the gases, naphtha and middle distillates. The bulk base oil fraction is then solvent dewaxed and stabilized using furfural refining followed by fractionation into the desired base oils [10,11,4]. Furfural extraction of the 875–1025°F distillate fraction was selected by Sun to overcome the poor hydrocracking response of the heavy distillate components of the hydrocracker feed. Extraction of the heavy distillate increases the yield and VI of the 100 neutral base oil. In addition, extraction of the heavy distillate reduced hydrogen consumption, reduced process severity

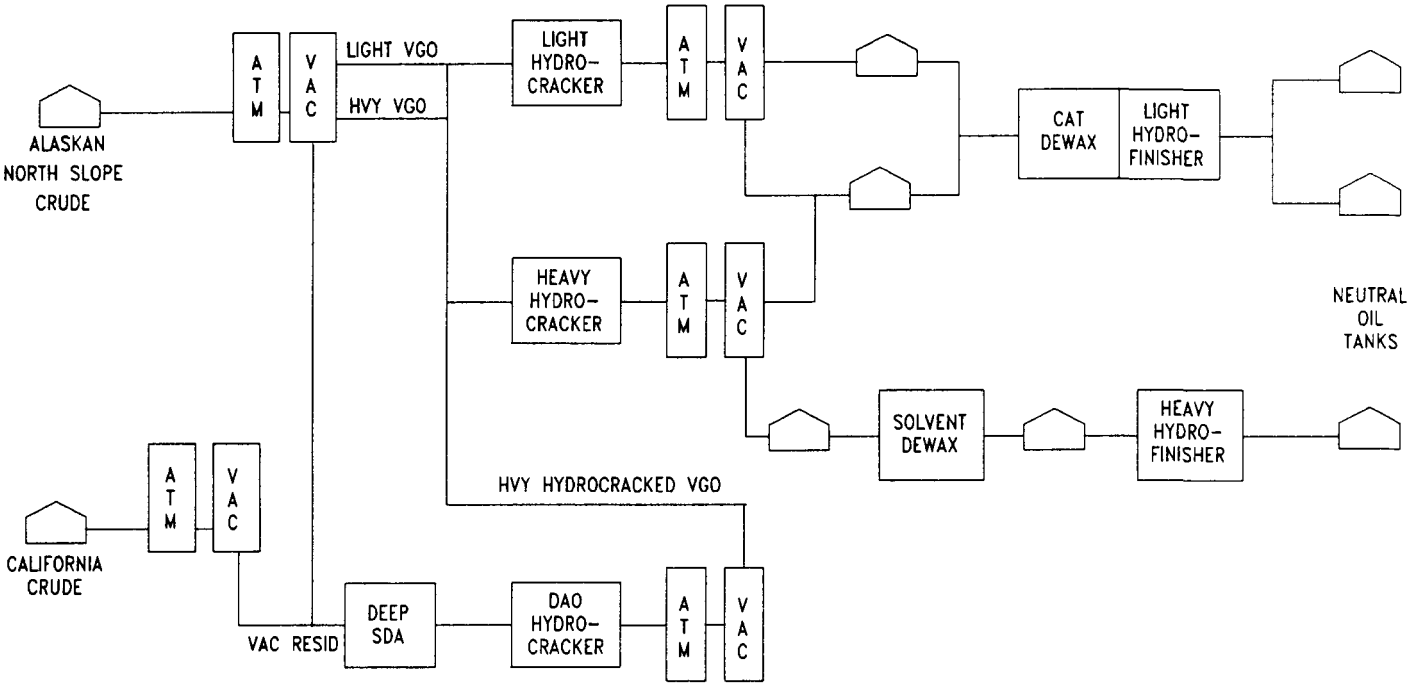

Figure 6.8 Simplified flow diagram of Chevron's Richmond Lube Oil Plant. (Reprinted from Ref. [23] by courtesy of Chevron International Oil Co.)

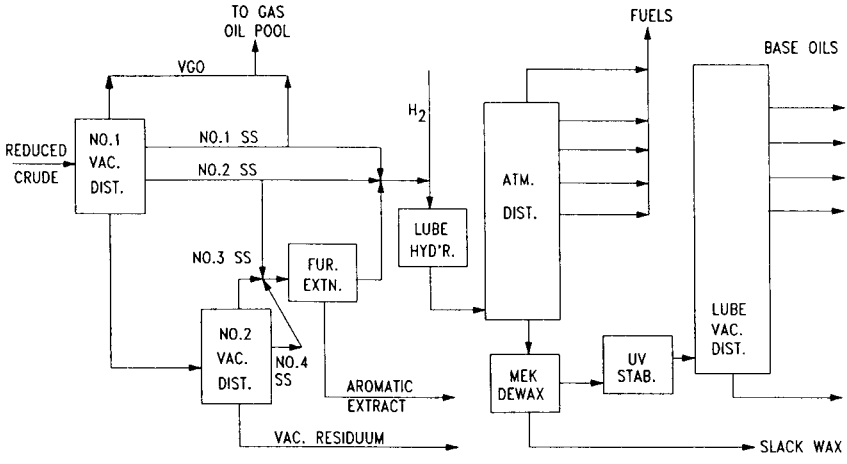

Figure 6.9 Simplified flow diagram of Sun's Yabucoa Lube Plant. (Reprinted from Ref. [11] p. 712 by courtesy of Sun Company, Inc.)

and doubled the liquid hourly space velocity thus reducing the reactor volume by 50 percent [10].

In contrast to other base oil refiners who use high pressure hydrogenation (hydrorefining) of the dewaxed oils, Sun selected furfural extraction to stabilize the hydrocracked oil against discoloration and sludging. Darkening and sludging may impair the quality of process oils and is detrimental to the quality of finished products such as textiles, rubber goods, etc. Poor light stability is not a problem in motor oil applications where additives containing dispersants are used [10].

British Petroleum, Nippon Petroleum Refining Company, Mitsubishi Oil Company, Modrica, and Wintershall manufacture very high VI base oils by solvent extracting and solvent dewaxing of hydrocracked distillates and/ or deasphalted oils [21,25,26,27,28]. Shell has developed and commercialized a combination process which uses mild furfural pre-extraction followed by moderately severe hydroprocessing and fractionation to manufacture some base oils [15]. This route, the Shell Hybrid or Hydroextraction Process, was selected to debottleneck existing solvent extraction plants and to permit manufacture of base oils with aromatic contents similar to that of solvent extracted base oils. It was also selected so that different additive packages would not be needed when severely hydrotreated base oils and solvent refined base oils are used to formulate products [15]. Shell reports that significant increases in base oil yield are obtained by varying the severity of the extraction [15]. Similar results have been reported by Bryer [10]. The data indicate that for a given base oil plant, extraction and hydrotreating conditions must be

optimized for each crude and feedstock being processed. Texaco has developed a combination process, Hy-Starting, which uses a severe hydrogen finishing process preceding solvent refining and solvent dewaxing to manufacture base oils. This process is being used commercially to increase the yield of base oils [29,30]. Hydrogen consumption is increased slightly in comparison to hydrogen finishing following solvent dewaxing. However, the size of the extraction unit is reduced and the need for installing finishing units for the manufacture of base oils or desulfurization of extracts (if needed) is eliminated or reduced in size. A comparison of hydrofinishing with Hy-Starting is provided in Table 6.13 [29,30].

The data in Table 6.13 show that the yield across solvent refining and solvent dewaxing increased when Hy-Starting was used. This type of processing is currently being used by some base oil refiners. Yanik, et al. [31] reported similar results when manufacturing base oils from base stocks derived from desulfurized atmospheric residues.

J. Wax Hydrocracking and Hydroisomerization

Shell has developed a process for the manufacture of extra high (145) VI base oils by hydrocracking and hydroisomerization of slack waxes followed by fractionation and solvent dewaxing [13,15]. Although details concerning the process conditions being used have not been disclosed, the patent literature indicates that a number of catalysts and a wide range of process conditions may be used; the published literature [15] reports that a proprietary catalyst is used. It is understood that this process is not available for license.

Releford and Ball [32] have reported that Exxon has developed and commercialized new base oils, EXXSYN, of about 140 VI. These oils are manufactured from slack wax using the processing sequence of (1) hydrotreating to remove the sulfur and nitrogen, (2) hydroisomerization to convert the wax to base oil, (3) hydrorefining to stabilize the base oils, (4) fractionation to remove

Table 6.13 Comparison of Hydrofinishing and Hy-Starting

	Arab heavy crude					
	Hydrofinishing process			Hy-started feedstocks		
Solvent neutral oil	Light	Medium	Heavy	Light	Medium	Heavy
Process yield, volume %						
Distillation	11.5	11.5	8.0	16	18	8.0
Furfural refining	56	54	52	65	70	62
Solvent dewaxing	75	74	74	77	76	76

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the light ends and (5) solvent dewaxing to remove unconverted wax. The uncoverted wax is recycled with the hydrotreated slack wax feed to the hydroisomerization reactor.

Chevron has announced the development of a catalytic dewaxing process which permits manufacture of very high VI base oils from slack waxes or from high wax content feedstocks [9,33]. The Chevron process is discussed in Chapter 8.

Although it is believed that at least two other refiners are currently using a wax isomerization process for the manufacture of very high VI base oils, a search of the literature does not confirm this. However, the patent literature reveals that several base oil refiners have developed processes for the manufacture of very high VI base oils by the hydrocracking and hydroisomerization of slack waxes and high wax content feedstocks.

K. Base Oil Composition and Performance [5,11,15,18,21,26,33]

Conventional VI, very high VI and ultra high VI base oils are currently being made using hydrocracking processes. Conventional VI base oils obtained from the hydrocracking processes closely resemble those of solvent extracted oils with the exception that aromatic, sulfur and nitrogen contents are usually lower and color is usually lighter at comparable VI and viscosity. The composition of base oils produced by a combination of hydrocracking and solvent extraction is more like that of the solvent refined base oils and these do not require modification of the additive packages [10,11,15]. Compositional data and a discussion of these base oils are presented in Chapter 2.

Performance of the hydrocracked base oils is equivalent to or better than that of the solvent refined oils in formulated products. However, it should be noted that hydrocracking removes some of the natural inhibitors and that stabilization is required if these oils are used in some process oils and speciality products.

L. Licensors of Base Oil Hydrocracking Processes

Licensors of the base oil hydrocracking processes include Chevron, IFP, Unocal and UOP. Some refiners use vacuum distillate fractions or the bottoms stream from fuels hydrocrackers as feedstocks to base oil plants for the manufacture of lubricant base oils.

M. Investment and Utility Requirements

The investment and utilities consumption for manufacture of base oils from Arabian Light feedstocks using Chevron Isocracking are summarized in Table 6.14 [34]. A comparison of the feedstock, investment, and utilities require-

Table 6.14 Investment Costs and Utilities for Isocracking Arabian Light Feedstocks

Basis BPSD Arabian Light feedstocks	5000 BPSD
On-site investment U.S. dollars/BPSD	4100
Utilities, typical per bbl feed:	
Fuel, 10^3 BTU	100
Electricity, kWh	3.0
Steam, 50 psig (net produced) lb	(10)
Steam, 150 psig, lb	27
Cooling water, gal	150

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ments for manufacture of lubricant base oils using the solvent extraction and IFP hydrocracking routes is presented in Tables 6.15 and 6.16 [17]. These data show that for a grassroots base oil plant (1) crude requirements are highest for the solvent extraction route and that investment, utilities and catalyst costs are highest for the hydrogen refining route. The results reported by IFP, a licensor of lube hydrocracking and solvent extraction processes, are in agreement with studies which have been made by other lube refiners and construction contractors. It should be noted that these comparisons were made using furfural as extraction solvent; the investment costs and utilities requirements would have

Table 6.15 Feedstock Requirements, Product, and By-Products for the Solvent and Hydrocracking Routes—Kuwait Crude

	Processing route	
	Solvent refining	Hydrogen refining
Feedstock, tons/year		
Reduced crude (380+ °C)	1,021,989	609,480
Products, tons/year		
150 solvent neutral	45,000	45,000
500 solvent neutral	75,000	75,000
Brightstock	30,000	30,000
By-products, tons/year		
Vacuum gas oil	179,392	121,009
Vacuum residuum	328,860	0
Asphalts	151,602	217,889
Extracts	169,665	0
Waxes	39,415	39,415
Diesel and naphtha	2,055	74,115

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Table 6.16 Investment Cost, Utilities, and Chemical Consumption for the Solvent and Hydrocracking Routes—Kuwait Crude

	Processing route	
	Solvent refining	Hydrocracking
Investment (France 1981)	U.S. dollars	
Vacuum distillation	7,500,000	5,100,000
Propane deasphalting	5,600,000	6,900,000
Furfural refining	8,700,000	—
Hydrogen refining	—	18,200,000
Solvent dewaxing	15,500,000	15,500,000
Hydrogen finishing	3,500,000	2,200,000
Steam reforming	—	6,200,000
Total investment	40,800,000	54,100,000
Utilities consumption		
Fuel, tons/hr	5.98	5.44
Electricity kwh/hr	4,465	6,455
Steam, tons/hr	36.1	36.8
Cooling water, M^3/hr	2,465	2,045
Chemicals consumption		
Solvents, tons/year	2,200	2,660
Hydrogen, tons/year	357	See Reformer Feed
Catalysts, U.S. $/year	18,500	199,500
Reformer feed, tons/hr	—	1.25
Steam production, tons/hr	—	7

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been even lower for use of N-methyl-2-pyrolidone as the extraction solvent; compare investment costs and utilities in Table 5.1.

Although these data indicate that hydrocracking is not cost-effective, it should be noted that hydrocracking will be more cost-effective for some refiners. The more economical process route depends on many factors which include 1) available crude source and its cost, 2) the final use and value of the by-products from the process, 3) availability of hydrogen and other process units, 4) desired product quality and 5) whether the plant is a stand-alone lube plant or is integrated into a fuels refinery. The use of both routes at different locations by Chevron, Gulf, Pennzoil, Sun and Quaker State are examples of base oil refiners that have selected different routes at different locations.

III. HYDROREFINING PROCESSES [6,35,36,37,38,39]

Hydrorefining processes often called speciality oil hydrotreating or hydrogenation processes operate at lower temperatures and at the same or somewhat

lower pressures than the hydrocracking processes. They are used 1) to saturate aromatics for the manufacture of speciality oils or 2) to stabilize or improve the quality of lube stocks from the lube hydrocracking processes.

A. Feedstocks

The feedstocks to the hydrorefining processes consist of, hydrocracked feedstocks, solvent extracted feedstocks and naphthenic distillates. White oils, mineral seal oils, roll oils, agricultural spray oils and other speciality oils can be manufactured from some solvent neutral oils and high quality naphthenic distillates with solvent extraction or hydrocracking being required to upgrade some of the lower quality feedstocks for use in speciality oil manufacture.

B. Processing Conditions [6,9,17,18,35,36]

The operating conditions of the hydrorefining processes depend on the composition of the feedstocks and catalyst used as well as end use of the base oils produced. The range of operating conditions is summarized in Table 6.17.

The higher pressure units are used for the stabilization of some but not all hydrocracked base oils. Hydrorefining of hydrocracked oils is usually conducted following solvent dewaxing or in the trailing reactor in a catalytic dewaxing unit.

C. Hydrorefining Catalysts

The catalysts used in the base oil and specialty oil hydrorefining processes are generally proprietary to the licensors of the processes and consist of the types listed in Table 6.18.

The nickel-tungsten catalysts are used most often for stabilizing base oils. The nickel-tungsten, nickel-molybdenum and cobalt-molybedum catalysts

Table 6.17 Speciality Oil Hydrorefining Process Conditions

	Operating conditions	
Process variable	Range	Typical
Pressure, psig	200–3000	1500–3000
Temperature, °F	480–850	500–600
Space velocity, Vo/Vc/hr	0.3–5.0	0.5–1.0
Hydrogen recycle, SCFB	550–8000	1000–3000
Hydrogen purity, mole %	90–100	90–95
Hydrogen consumed, SCFB	50–3000	100–1000
Yield, volume %	80–100	95–98
Catalyst life, years	1–3	1–2

Table 6.18 Lube Hydrorefining Catalysts

Nickel–molybdenum on alumina
Nickel–tungsten on silica alumina
Nickel–tungsten on alumina (most common)
High nickel (Low sulfur and nitrogen content feedstocks)
Platinum (Low sulfur and nitrogen feedstocks)
Palladium (Low sulfur and nitrogen feedstocks)

with or without activity promoters are used in some lube and wax hydrorefining processes with the nickel and the precious metal catalysts being used for manufacture of medicinal grade white oils. A listing of some but not all of the commercially available hydrorefining catalysts is provided in Table 6.19; this listing was prepared from information reported in the *Oil and Gas Journal* [19,20].

D. Process Variables

The process variables for lube hydrorefining processes are listed in Table 6.20. These are the same process variables as those of the hydrocracking and hydrogen finishing processes; the main difference is that the operating pressure is

Table 6.19 Commercially Available Lube Hydrorefining Catalysts

		Composition		License
Supplier	Name	Metals	Support	required
Akzo	KF-330	Nickel–tungsten	Alumina	No
	KF-843	Nickel–molybdenum	Alumina	No
BASF	H 1-80	Nickel	Silica	No
	H 8-21	Nickel–molybdenum	Alumina	No
Chevron	ICR-403	Proprietary	Proprietary	Yes
	GC-26	Proprietary	Alumina	No
Criterion	C-614	Platinum	Silica–alumina	No
	C-624	Platinum/palladium	Silica–alumina	No
	C-874A	Nobel metal	Alumina	No
	HDS-9	Nickel–molybdenum	Alumina	No
Crosfield	594	Nickel–molybdenum	Alumina	No
	599	Nickel–molybdenum	Alumina	No
Engelhard	NI-4342	Nickel–tungsten	Alumina	No
	NI-4352	Nickel–tungsten	Alumina	No

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Table 6.20 Lube Hydrorefining Process Variables

Feedstock	Pressure
Temperature	Space velocity
Catalyst	Hydrogen purity
Recycle hydrogen rate	

higher for the hydrocracking processes and lower for hydrogen finishing and operating temperatures and hydrogen recycle rates are lower for hydrogen finishing and equivalent to or higher for hydrocracking. Operation of the hydrorefining processes at higher temperatures would result in hydrocracking reactions, the breaking of carbon-to-carbon bonds and significant viscosity reductions which are undesirable in the hydrorefining operation.

1. Effect of Feedstock Quality

The yield of base oil depends on the quality of the feedstock and base oil specifications, catalyst and process severity. Since hydrorefining is usually conducted using a fully refined and dewaxed base oil, the yield is usually on the order of 95 to 100 percent basis feed. Feedstocks which are high in sulfur, nitrogen and/or aromatic content provide lower yields and are usually processed in the two-stage hydrorefining units. White oil hydrorefining processes are usually operated at lower pressure than the processes used to stabilize hydrocracked oils. The typical range of operating conditions for the IFP-TOTAL white oil hydrorefining process are listed in Table 6.21 [17]. The catalysts used in the IFP-TOTAL process consist of nickel–molybdenum on alumina in the first stage and a noble metal catalyst in the second stage [38].

Typical operating conditions for the BASF white oil hydrorefining processes are listed in Table 6.22 [36]. Although the hydrogen recycle rate and hydrogen consumption have not been reported and will depend on the quality of the feedstock, the ranges for the hydrogen recycle rate is most probably in the range of 3000 to 6000 SCF per barrel and the hydrogen consumption is in the range of about 50 to 100 SCF per barrel of feed.

Table 6.21 Typical IFP-TOTAL White Oil Hydrogenation Conditions

Total pressure, psia (bars)	1700–2400	(120–170)
Temperature, °F (°C)	570–680	(300–360)
Space velocity, LHSV	0.3–1.0	
Hydrogen recycle, SCFB (M^3/M^3	2970–5933	(500–1000)
Hydrogen consumption, SCFB (M^3/ton)	50–110	(60–130)

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Table 6.22 Typical BASF White Oil Hydrogenation Conditions

	First stage	Second stage
Catalyst	Nickel–molybdenum	Nickel
Pressure, psig (MPa)	1160–2900 (8–20)	1450–2900 (10–20)
Temperature, °F (°C)	572–716 (300–380)	392–572 (200–300)
Space velocity	0.1–1.0 kg/l/hr	0.1–0.5 kg/l/hr

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The single stage hydrorefining processes are used for the manufacture of technical grade white oils and for manufacture of such products as waxes, agricultural spray oils, mineral seal oils, etc. In this process the sulfur and nitrogen are removed and the aromatics are reduced to very low levels [6,17,35,36].

The two stage processes are most often used to prepare pharmaceutical and food grade white oils. The feedstock to the second stage hydrorefining unit is the effluent from the first stage. The second stage treatment saturates the last traces of aromatics [6,17,35,36].

Typical results for the hydrorefining of technical grade white oil using the IFP-TOTAL single stage process are shown in Table 6.23 [38]. These data show that the U.S. FDA requirements were met for all three grades of oil. A summary of the technical grade white oil and medicinal grade white oil specifications is presented in Tables 2.26 and 2.27 of Chapter 2.

The results for manufacture of food grade white oils from three feedstocks are summarized in Table 6.24. A comparison of the data in Tables 6.23 and 6.24 show that the change in physical properties is greatest for the higher viscosity oils. This change in physical properties occurs in the first stage and practically no change in physical properties occurs in the second stage [6,17,35]. The yield is usually 99 percent or higher for these processes [6,17,35].

IFP has reported development of a first stage hydrocracking type catalyst which permits manufacture of food grade white oils with a small decrease in product yield [38]. Results for this type of operation are shown in Table 6.25.

2. Effects of Temperature and Space Velocity

The process temperature and space velocity (LHSV) are the primary process variables which affect base oil or wax yield. The use of low space velocity and low temperature is usually preferred over high space velocities and high temperatures. Excessively high temperatures increase the amount of extraneous cracking and coke deposits on the catalyst which lead to short catalyst life and poor color stability of the finished oil.

Table 6.23 Hydrorefining for Technical Grade White Oils

	Light oil		Medium oil		Heavy oil	
	Feed	Product	Feed	Product	Feed	Product
Density at 15°C	0.859	0.845	0.8845	0.8614	0.888	0.8675
Viscosity cSt @ 100°F	21.6	19.45	82.98	45.96	148	90.6
@ 210°F	4.18	3.94	9.35	6.83	13.56	10.39
Viscosity index	105.5	107	97	114	94	106
Flash, COC°F	204	202	256	212	274	252
Pour point, °C	−15	−12	−12	−6	−9	−3
Sulfur, ppm	7400	<0.5	9500	5	10,100	7
Saybolt color	> +20[a]	+25		+30	4.5(b)	+27
Aromatics, wt %						
Monoaromatics			20.9	2.39		
Diaromatics			4.37	0.029		
Polyaromatics			2.39	0.022		
Direct UV absorbance						
260–280 NM	1.8145	0.0403			2.946	0.098
280–290 NM	1.0161	0.0306			1.762	0.084
290–300 NM	0.6828	0.0078			1.238	0.028
300–360 NM	0.4725	0.0058			0.941	0.021
360–400 NM	0.0045	0.0018			0.037	0.002
FDA, ASTM D 2269						
272 NM				0.35		
280 NM 4.0 max[a]				0.36		
284 NM 3.3 max[a]				0.385		
300 NM 2.3 max[a]				0.26		
305 NM				0.34		
320 NM 0.8[a]				0.14		
350 NM				0.200		

[a] U.S. Specification
[b] ASTM Color
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E. Process Flow

A simplified flow diagram for a hydrorefining unit used for the stabilization of hydrocracked oils and manufacture of speciality oils and waxes is shown in Figure 6.10 [35,36,38]. Operation of these units is essentially identical to that of the hydrocracking processes with the exception that a hydrogen quench is not required and a simple stripper is used to remove the small amount of light materials from the hydrorefined oil.

Table 6.24 Hydrorefining Food Grade White Oils

	Light oil		Medium oil		Heavy oil	
	Feed	Product	Feed	Product	Feed	Product
Density at 15°C	0.8621	0.8487	0.8845	0.8606	0.888	0.858
Viscosity cSt @ 100°F	20.83	18.08	82.98	64.22	148	75.3
@ 210°F	4.02	3.77	9.35	8.40	13.56	9.45
Viscosity index	99	107	97		94	113
Flash, COC°F	216	194	256		274	244
Pour point, °C	−12	−12	−12	−6	−9	−3
Sulfur, ppm	5670	<0.5	9500	7.3	10,100	<0.5
Saybolt color		+30		+30	4.5(b)	+37
Aromatics, wt %						
Monoaromatics	17.6	0.059	20.9	0.059		
Diaromatics	1.86	0.003	4.37	0.002		
Polyaromatics	0.80	0.006	2.39	<0.001		
Direct UV Absorbance						
260 NM		0.53		0.40		
272 NM 1.6[a]		1.01		0.81		0.98
290 NM 0.20[a]		0.11		0.12		<0.01
300 NM 0.15[a]		0.06		0.07		<0.01
310 NM		0.03		0.04		
325 NM		0.01		0.01		
FDA, ASTM D 2269						
260 NM 0.10[a]		<0.005		0.01		
280–300 NM 0.10[a]		0.001		0.015		
320 NM 0.10[a]		<0.005		0.01		
340–380 NM 0.10[a]		<0.005		0.005		
400–420 NM 0.10[a]		<0.005		<0.005		
Carbonizable Substances, 4[a]	>16	<3	>16	4		<3

[a] U.S. Specifications, maximum value

[b] ASTM Color

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Some refiners and licensors use two reactors in series which may contain the same or different catalysts in each reactor. However, most of the two stage processes use two single stage hydrorefining units operated in series (see Figure 6.11) with the effluent from the first unit being used as the feed to the second unit for the manufacture of medicinal grade white oils. Most of the sulfur and nitrogen are removed and most of the aromatics are converted to saturates in the first stage using bimetallic catalysts while the last traces of aromat-

Table 6.25 Hydrocracking for White Oil Manufacture

		First stage		Second stage	
	Feed	Standard catalyst	Cracking catalyst	Standard catalyst	Cracking catalyst
Density at 15°C	0.8619	0.8445	0.834		
Viscosity cSt @ 100°F	21.63	19.3	15.05		
@ 210°F	4.02	3.77	9.35		
Viscosity index	105	105	108		
Flash, COC°F	206	194	188		
Pour point, °C	−15	−12	−12		
Sulfur, ppm	6400	11	9		
Aromatics, wt %					
Monoaromatics	13.8	1.91	0.76	0.78	
Diaromatics	1.86	<0.035	0.035		
Polyaromatics	1.00	<0.035	<0.035		
Direct UV absorbance					
260 NM		>20	12.6	0.72	0.04
272 NM 1.6[a]		>20	18.5	1.32	0.065
290 NM 0.20[a]		3.70	9.8	0.04	0.010
300 NM 0.15[a]		2.30	5.75	0.038	0.005
310 NM		1.40	4.0	0.022	0.005
325 NM		0.52	2.8	0.005	0.005
FDA, ASTM D 2269					
260 NM 0.10[a]				0.04	0.005
280–300 NM 0.10[a]				0.012	0.005
320 NM 0.10[a]				0.008	0.005
340–380 NM 0.10[a]				0.005	0.005
400–420 NM 0.10[a]				<0.005	0.005
Carbonizable					
Substances, 4[a]				2	<1

[a] U.S. Specifications, maximum value

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ics are converted to saturates and the other impurities are converted in the second stage using nickel or precious metal catalysts [6,35,36,38].

F. Licensors of Hydrorefining Processes

Licensors of the lube hydrorefining processes include BASF, IFP, Chevron, Lyondell and UOP. In addition, several refiners use their own processes and some engineering firms and catalyst manufacturers provide technical informa-

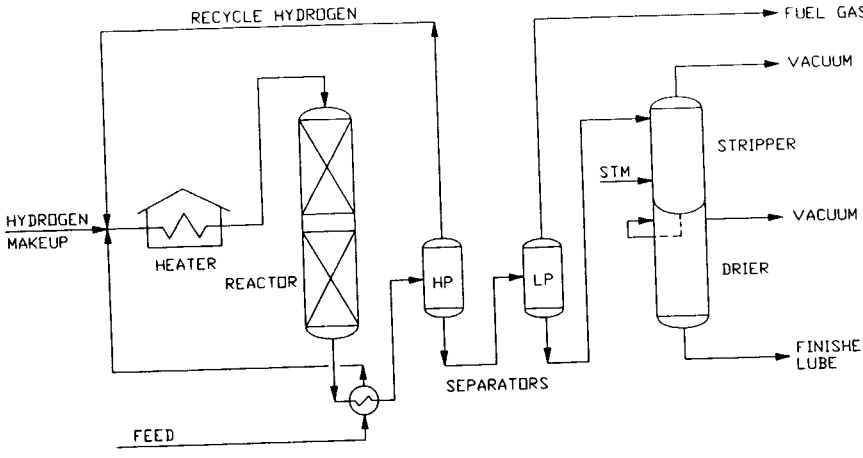

Figure 6.10 Single stage base oil hydrorefining unit. (Reprinted from Ref. [17], p. 171 by courtesy of Institut Francais du Petrole.)

tion on the use of their catalyst for the hydrogenation of speciality products and solvents.

G. Investment and Utility Requirements

Investment for a hydrorefining process is approximately the same as that of a vacuum gas oil hydrotreater and will range from about 1000 to 2000 U.S. dollars per barrel of feed for 2000–5000 BPSD units constructed on the U.S. Gulf Coast. The investment and utilities requirements for hydrorefining for white oil manufacture are summarized in Table 6.26 [38].

Table 6.26 Hydrorefining Investment and Utility Requirements

Feed	Macro wax	Dewaxed oil	Dewaxed oil
Product	Food grade wax	Technical white oil	Food grade white oil
Feed capacity, tons/year	20,000	20,000	20,000
Investment, MM francs(1979)	7	9	14
Utilities			
Electricity, kwh/h	70	120	200
Fuel, kcal/hour	160,000	200,000	220,000
Steam, ton/hour	1.2	1.2	2.4
Cooling water, m^3/hr	100	100	170
Hydrogen consumption, NM^3/hr	40	200	325
Yield	99	85–95	85–95

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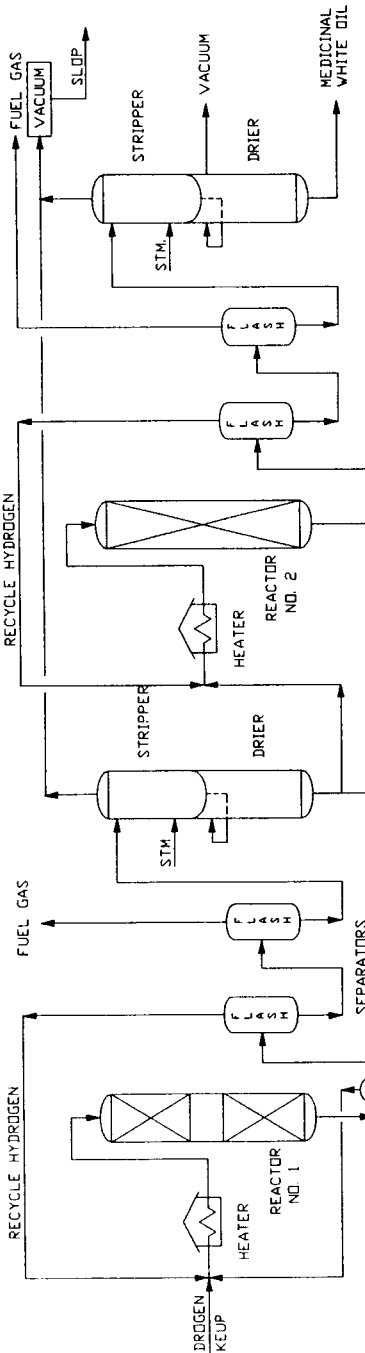

Figure 6.11 Two-stage base oil hydrorefining unit. (Reprinted from Ref. 17, p. [17] by courtesy of Institut Francias du Petrole.)

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7

Solvent Dewaxing and Wax Deoiling Processes

I. INTRODUCTION

The raw paraffin distillates and residual oils leaving the crude stills contain wax and are normally solids at ambient temperature. The deasphalting and refining processes concentrate the wax in the base oil feedstocks. Removal of wax from these fractions is necessary to permit manufacture of lubricating oils with the desired low temperature properties. Although the cold settling–pressure filtration processes and centrifuge dewaxing processes have for the most part been replaced by solvent dewaxing, these older processes are still used to a limited degree.

A considerable number of solvent based processes have been developed over the years for the dewaxing of lubricating oils. These processes can be divided into three basic sequential steps; 1) crystallization—the dilution and chilling of the feedstock with solvent, 2) filtration of the wax from the solution of dewaxed oil and solvent and 3) solvent recovery from the wax cake and filtrate for recycle in the process by flash distillation and stripping. The major process variables include 1) the nature of the feedstock, 2) the solvent and solvent composition, 3) the solvent dilution procedure, 4) the chilling procedure, 5) the filtration procedure and 6) the solvent recovery method. The manner in which the above variables are controlled can have a significant effect on 1) the production rate, 2) yield of dewaxed oil, 3) the pour point of the dewaxed oil, 4) the oil content of the wax and 5) the investment and operating costs. The

major processes in use today are the 1) Edeleanu Di/Me Process, 2) the ketone dewaxing processes and 3) the propane dewaxing process. The urea dewaxing processes are similar to the solvent dewaxing processes and will also be discussed.

A. Purpose and Effects of Solvent Dewaxing and Wax Fractionation

The purposes of solvent dewaxing and wax fractionation processes are summarized as follows.

The purpose of the solvent dewaxing process is the removal of wax from lube feedstocks and the improvement of the low temperature properties of lubricating oil base stocks.
The purpose of the wax fractionation process is the removal of oil and low melting point waxes to permit manufacture of low oil content waxes with high melting points.

The effects of solvent dewaxing on the properties of feedstock in comparison to the dewaxed oil are 1) a decrease in wax content, 2) an increase in aromatic content, 3) a decrease in pour point, 4) an increase in nitrogen content, 5) a decrease in API Gravity, 6) an increase in sulfur content, 7) a decrease in viscosity index and 8) an increase in viscosity.

The primary effect of the wax fractionation processes is to decrease the oil content of the wax and to increase in the melting point of the wax.

B. Feedstocks and Products

The feedstocks and products for the solvent dewaxing and wax deoiling processes are listed in Table 7.1. These are general terms for the feedstocks

Table 7.1 Solvent Dewaxing and Wax Deoiling Feedstocks and Products

Dewaxing feedstocks	Dewaxing products
Solvent extracted distillates	Solvent neutral oils
Solvent extracted DA oils	Bright stocks
Deasphalted (DA) residua	Cylinder oils
Hydrocracked distillates	Solvent neutral oils
Hydrocracked DA residua	Bright stocks and neutrals
Unrefined distillates	Paraffin pale oils
Wax deoiling feedstocks	Deoiling products
Slack waxes	Hard wax & soft wax
Waxy distillates	Hard wax & soft wax

and the products for which one may find other designations. Solvent extracted oils are most often called raffinates or refined oils. Solvent neutral oils are sometimes called filtrates, pressed oils, neutral oils, solvent neutral oils, bright stocks, spindle oils, hydraulic oils, turbine oils, refrigeration oils or transformer oils depending on the processing used or their intended end use.

The by-products from the manufacture of lubricating oil base stocks consist of different types of wax which are defined differently among manufacturers. The names that follow will therefore be used throughout this discussion in referring to the different oil content waxes obtained from solvent dewaxing and wax deoiling operations.

Solvent Dewaxing By-Products

Name	Oil content, wt %
Slack wax	5 to 50
Scale wax	1 to 5
Hard wax, distillate	< 0.5
petrolatum	<0.5 to 1.0
Soft wax (By-product from hard wax manufacture)	

Slack wax and scale wax are the by-products from solvent dewaxing used as the feedstocks to wax fractionation. Hard wax and soft wax are the product and by-product from the wax fractionation process. Soft wax is the by-product or intermediate fraction (a mixture of oil and low melting point wax) with a pour or melting point between that of the dewaxed oil and hard wax. Hard wax is the low oil content–high melting point product from wax fractionation.

II. SOLVENT DEWAXING AND WAX DEOILING PROCESSES

A. Ketone Dewaxing Processes

The ketone dewaxing processes are suitable for dewaxing the entire range of lube stocks. These processes are based on improvements which have been made to the original ketone dewaxing process, the Acetone–Benzol Process (A–B process) which was commercialized in 1927 and has been most extensively developed by Texaco [1]. The original ketone process sometimes called the "conventional" or "classical" solvent dewaxing process was a single dilution–single stage filtration process which has been modified to use various mixtures of acetone, benzene, methyl ethyl ketone (MEK), methyl isobutylketone (MIBK), toluene and other aromatic hydrocarbons. The solvent mixtures used most often are MEK–toluene and MEK–MIBK with neat MIBK being used in some cases. Improvements made to the ketone dewaxing processes

over the years include 1) continuous crystallizers and scraped-surface exchangers as a replacement for batch chillers, 2) rotary vacuum filters as replacements for the pressure type filters, 3) use of synthetic filter cloth in place of cotton canvas for longer on stream time, 4) multiple dilution and filtration techniques, 5) multiple effect evaporation for solvent recovery, 6) inert gas in place of steam for stripping, 7) cold backwashing as a replacement for hot washing of the filters and 8) improved refrigeration plants and techniques. In addition, these processes have been modified and used to deoil waxes using recrystallization and warm-up deoiling techniques. Although some refiners use the older double dilution–single stage filtration procedures or modifications of these processes described in the literature, the most widely used ketone dewaxing processes in use today are the Texaco Solvent Dewaxing Process and the Exxon Dilchill™ Process.

1. The Texaco Solvent Dewaxing Process [1–9]

This process is commonly called the MEK or ketone dewaxing process, an extractive–crystallization process, is the most widely used dewaxing process in the petroleum industry. Today there are over 120 Texaco licensed MEK Dewaxing Units in operation in more than 20 different countries. The Texaco Wax Fractionation Process (using the warmup deoiling or recrystallization procedures) is also used in conjunction or separate from the MEK dewaxing process by many of these licensees for the manufacture of low oil content hard or finished waxes. The process flow for this process is shown in Figure 7.1 [2] and consists of the three basic sequential processing steps listed as follows.

a. Crystallization (dilution and chilling of the feedstock).
b. Filtration (separation of wax and dewaxed oil filtrate).
c. Solvent recovery (separation of solvent from wax and oil).

The specific manner in which each of these steps is conducted and feedstock properties can have a significant effect on the economics of the process.

The waxy feedstock is heated to 10–15°F above the cloud point of the oil and diluted with solvent while chilling at a controlled rate in double- pipe scraped-surface exchangers and chillers. Two to four volumes of solvent are used per volume of feed. The incremental or multiple dilution procedure is used for low- to medium-viscosity stocks and a double dilution controlled shock chilling procedure is used for high viscosity stocks in the more modern units. The older double-dilution single-stage filtration procedure is still used in some units. About 60 percent of the chilling is obtained by heat exchange between the feedstock and solvent with the cold filtrate from filtration being used as the chilling medium in the annulus of the double-pipe exchangers. The remainder of the refrigeration required for chilling is obtained by indirect heat exchange with a refrigerant in the annulus of the double-pipe chillers. The slurry leaving the chillers at a temperature of 5 to 20°F below the desired pour point is filtered using rotary vacuum filters and the wax cake is washed with a

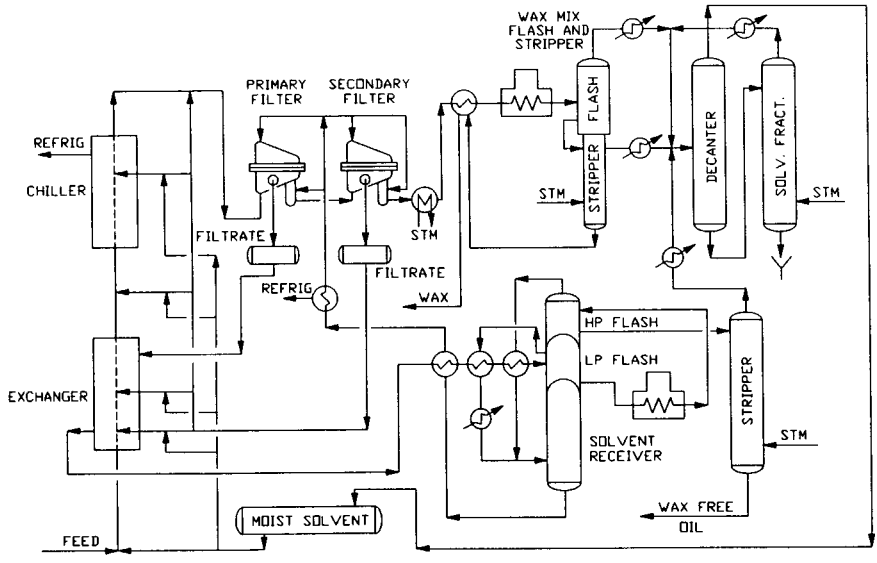

Figure 7.1 Process flow diagram of the Texaco Solvent Dewaxing Process. (Reprinted from Ref. [2] by courtesy of Texaco, Inc.)

spray of cold solvent before being discharged by an inert gas blow back. The filtrate from these primary filters is used to prechill the feedstock and solvent mixture in the scraped-surface exchangers. The filtrates from these filters may be separated into a primary (oil rich) filtrate used as the chilling medium and the wash (oil lean) filtrate used as dilution solvent. The wax cake from the primary filter is diluted with additional solvent and filtered in a second (repulp) rotary vacuum filter with cold solvent washing of the wax cake to reduce the oil content of the wax. The filtrate from the repulp filter is normally used as dilution solvent in the crystallization train but may also be separated into an oil rich filtrate for use as dilution solvent and an oil lean filtrate for dilution of the wax from the primary filter. The solvent is recovered from the resultant dewaxed oil filtrate and wax cake by dual but preferably triple-effect flash vaporization and recycled in the process. The wax recrystallization and wax warm-up deoiling procedures are used in those cases in which the lube refiner also manufactures a hard or finished wax. These processes are discussed under the section on wax deoiling processes.

2. The Exxon Dilchill™ Dewaxing Process [5,7,10,11,12,13]

This process is a modification of the ketone dewaxing process. The process flow is essentially that of a ketone dewaxing unit with the exception that a special crystallizer is used in place of the scraped-surface exchangers. Direct chil-

ling of the feedstock in the crystallizer is accomplished using a cold-solvent multiple-dilution shock-chilling technique in a highly sheared environment. This high degree of mixing is used as a means of overcoming the poor filtration obtained with the conventional shock chilling techniques. A solvent drying step must be added to remove the last traces of water from the solvent to prevent the icing of the solvent chillers during chilling of the solvent to the low temperatures required for direct chilling of the feedstock. Scraped-surface chillers using indirect refrigeration for chilling are used to complete the chilling of the solvent–feedstock mixture to the filtration temperature. Filtration and solvent recovery by multiple effect evaporation are conducted in the usual manner.

Eagen et al. [11] have reported an increase in filtration rate of 40 to 50 percent and a decrease in the solvent to oil ratios of 10 to 30 percent for Dilchill dewaxing as compared to conventional MEK dewaxing. Sequeira [20] has reported similar increases in filtration rate and equivalent to greater reductions in solvent to feed ratio for incremental dilution and controlled shock chilling MEK dewaxing as compared to conventional MEK dewaxing.

The warm-up wax deoiling procedure described in the section on wax deoiling is used in conjunction with the Dilchill™ process.

B. The Di/Me Dewaxing Process

The Di/Me process which uses a mixture of dichloroethane (Di) and methylene dichloride (Me) as the dewaxing solvent was developed by Edeleanu Gellschaft mbH. It is used by a few refineries in Europe for both the dewaxing of lubricating oil base stocks and the manufacture of low oil content waxes [5,14]. A simplified flow diagram is shown in Figure 7.2 [14].

The warm waxy feed is dissolved in the Di/Me solvent and cooled to the initial wax crystallization temperature with water in shell and tube heat exchangers and with cold filtrate in scraped-surface double-pipe exchangers wherein about 60 percent of the cooling is conducted. The remaining 40 percent of the cooling is conducted in scraped-surface double-pipe chillers using ammonia or propane refrigeration. The waxy slurry from the chillers is filtered in rotary vacuum filters and the wax cake is washed with cold solvent. The oil rich filtrate from the primary filter is used to prechill the feed in the scraped surface exchangers and the oil lean wash filtrate is used as a second dilution in the chilling train. The wax cake from the primary filter is diluted with the oil lean filtrate from the second stage filter and the repulped mixture filtered in the second stage (repulp) filter. The products from the repulp filter are a soft wax filtrate and hard wax cake. The second stage is omitted if hard wax production is not desired. The solvent dewaxed oil, soft wax and hard wax are recovered by multiple effect evaporation. The recovered solvent is recycled in the process.

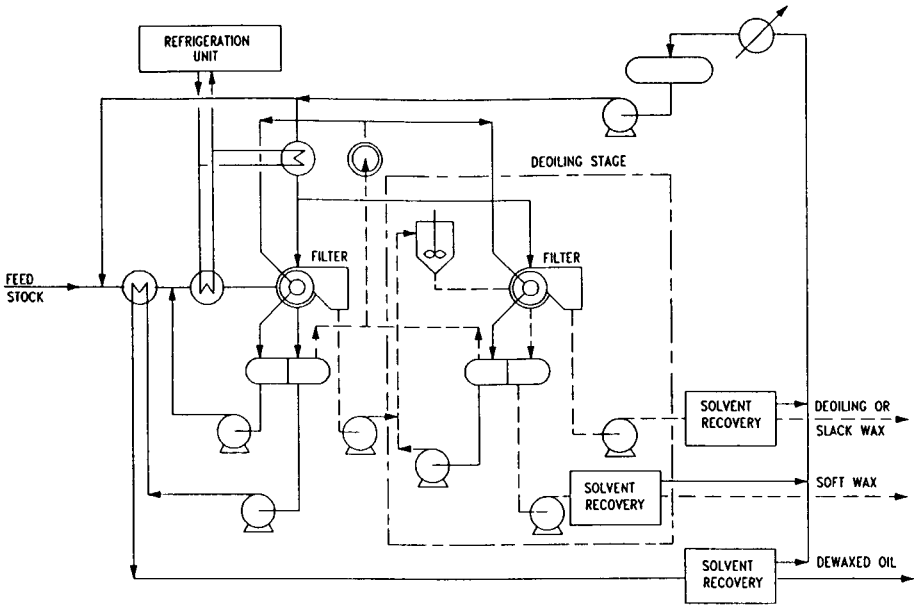

Figure 7.2 Process flow diagram of the Di/Me Dewaxing Process. (Reprinted from Ref. [14] by courtesy of Edeleanu.)

C. The Propane Dewaxing Process

The propane dewaxing process was developed and first used in 1932 by Standard Oil Company of Indiana and further improved by the JUIK (Standard Oil of New Jersey, Union Oil Co., Standard Oil of Indiana and M. W. Kellogg) patent combine [4]. A simplified flow diagram for this process is shown in Figure 7.3 [5].

The feedstock is diluted with two to four volumes of propane and heated to a temperature where all the wax is dissolved. The mixture of propane and feedstock are then cooled to the cloud point by water cooling in shell and tube heat exchangers and then cooled to the filtration temperature at a rate of 1 to 2°F per minute by direct evaporation of the propane from the mixture in parallel evaporative chillers. Additional cold propane is added to replace solvent vaporized during chilling and to control the viscosity of the slurry which is filtered in rotary vacuum filters operated under pressure. Cold propane is used to wash occluded oil from the filter cake. Recovery of the solvent for recycle in the process is usually conducted by vaporization in two or more evaporators and by stripping. Advantages for this process are 1) the solvent is cheap and

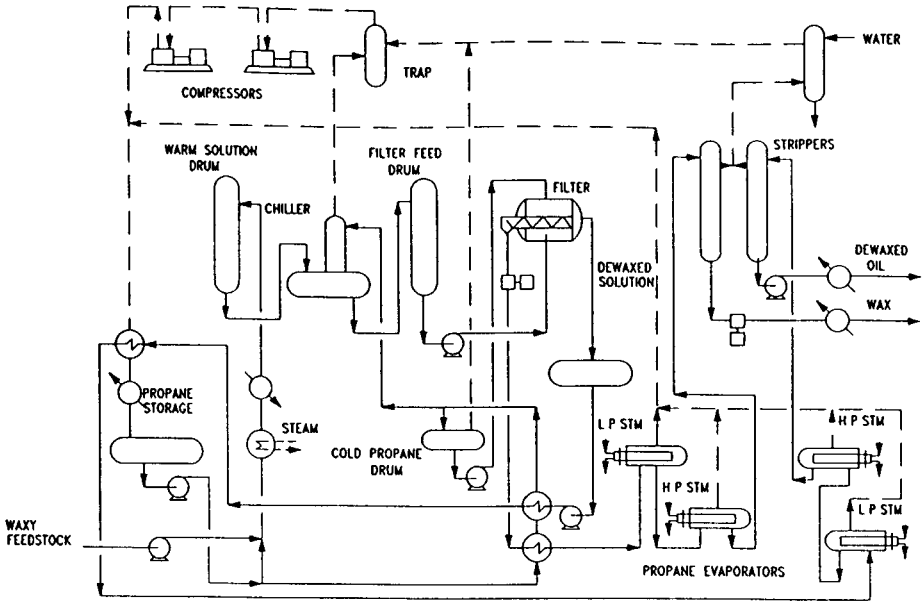

Figure 7.3 Process flow diagram of the propane dewaxing process. (Reprinted from Ref. [7], p. 354.)

readily available in most refineries, 2) use of evaporative chilling greatly reduces the adhesion of wax to the crystallizer walls and eliminates the need for expensive crystallizers and 3) wax cloud points of propane dewaxed bright stocks are usually lower as compared to ketone dewaxed bright stocks. The disadvantages for the use of propane as a dewaxing solvent are that 1) the dewaxing differential (25–45°F) is considerably higher than that of the ketone dewaxing or Di/Me dewaxing processes, 2) control of batch chilling is difficult because the compressors are under utilized during the initial chilling phase of the process and 3) dewaxing aids are required to obtain good filtration rates [4,5].

The use of ketone solvents as a wax antisolvent in combination with propane has been proposed for improving the economics of the propane dewaxing process and in one case the use of propylene and acetone as the dewaxing solvent was tested commercially [11]. Although this test was reported to be successful, it is not known if the modified process is being used commercially.

D. The Urea Dewaxing Procesess [16,17,18,19]

The urea dewaxing processes are normally not thought of as a solvent dewaxing process. However, considerable quantities of solvent are used in the

process. The formation of crystalline complexes (adducts) between urea and straight chain hydrocarbons was discovered by Bergen in 1940 and has been used as a basis for lube oil dewaxing processes and for the manufacture of normal paraffins. The hexagon crystalline structure of urea contains channels having an inside diameter of 4.7 angstroms in which normal paraffins with six or more carbon atoms can be occluded. The spiral-like nature of the complex formed also permits occlusion of branched hydrocarbons if the hydrocarbon has a long unbranched chain. Although urea can be used to remove the normal paraffins by mixing the urea with the oil to be processed or by percolation of the oil through a bed of crystalline urea, it is most often used with an activator (alcohol, ketone or chlorinated hydrocarbon) solvent. A very comprehensive review of the fundamentals and the use of urea as a solvent for the dewaxing of base oil stocks and the manufacture of n-paraffin waxes has been reported by Hoppe [17]. The use of urea dewaxing on a commercial scale for the manufacture of base oils and waxes was developed by Edeleanu and was first used commercially in 1954 by Deutche Erdoel A.G. in Heide, Germany. This process, depicted in Figure 7.4, was used for both the manufacture of very low pour point oils and/or high purity waxes from paraffinic feedstocks.

The waxy feedstock is intimately mixed with urea and methylene chloride or dichloromethane in a series of reaction vessels and cooled to the desired temperature for adduct formation by evaporating a portion of the activator solvent.

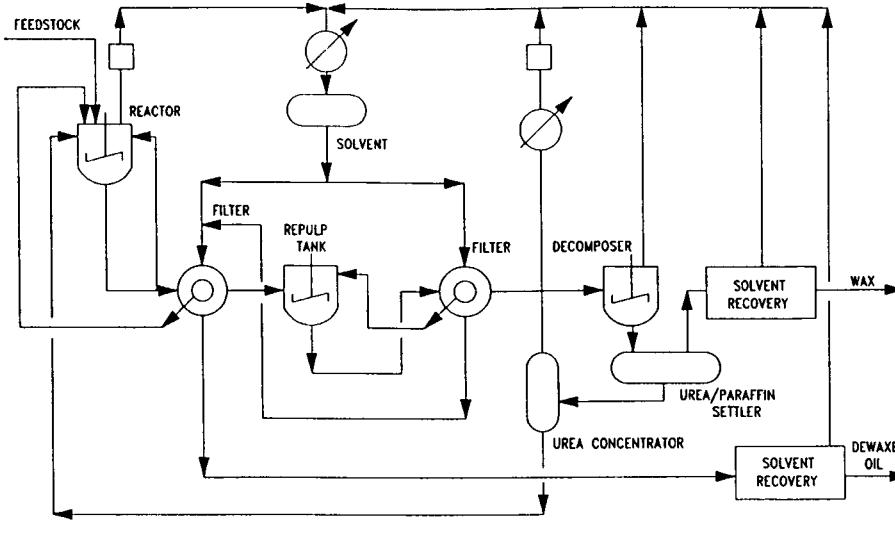

Figure 7.4 Process flow diagram of the urea dewaxing process. (Reprinted from Ref. [18] by courtesy of Edeleanu.)

The slurry thus formed is separated into an adduct cake and dewaxed oil filtrate using a specially designed pan or rotary filter where the adduct is washed with additional solvent to remove occluded oil. The adduct is decomposed into an aqueous urea solution and a wax phase by the addition of water and heat. The urea is filtered, dried and recycled in the process. The solvent is recovered from the dewaxed oil by multiple effect evaporation and stripping. The solvent from the multiple effect evaporators and the solvent, after drying, are recycled in the process.

The urea dewaxing processes are suitable for separating normal paraffins from other types of hydrocarbons. However, urea is not very selective for the removal of long chain branched hydrocarbons; urea will remove hydrocarbons containing branches and rings providing the molecule contains a long unbranched chain [19]. Information concerning other urea dewaxing and wax manufacturing processes has been reported by Hoppe [13] and Scholten [19].

III. WAX FRACTIONATION (DEOILING) PROCESSES

The specifications for finished waxes depend on their end use which determines the degree of refining required. Reducing the oil content to low levels (0.1 to 1.0 %) is accomplished by removing the last traces of oil from the wax (deoiling) and obtaining the specified hardness (penetration) by controlling the melting point. Since these operations are conducted at the same time using the same equipment and procedures, the process is sometimes called wax deoiling and at other times wax fractionation.

The commercial wax deoiling or fractionation processes are 1) the sweating process, 2) the recrystallization process, 3) the warm-up deoiling process and 4) the spray deoiling process.

A. The Wax Sweating Process [1]

This process is the oldest wax deoiling process which has for the most part been replaced with the more modern processes. In this process, the molten wax is solidified by chilling in large pans contained in large ovens. The wax is slowly heated in these ovens wherein the oil and lower melting point (soft) wax are separated (sweated) from the higher melting point (hard) wax. This process can be used for the deoiling of the paraffin (macrocrystalline) wax but cannot be used with the waxes which contain microcrystalline wax or petrolatums [1].

B. The Warm-up Deoiling Processes [2,5,9,10]

A simplified process flow diagram for the warm-up wax deoiling processes is shown in Figure 7.5 [19]. These processes are always operated in conjunction with the solvent dewaxing processes; the slack wax from solvent dewaxing is

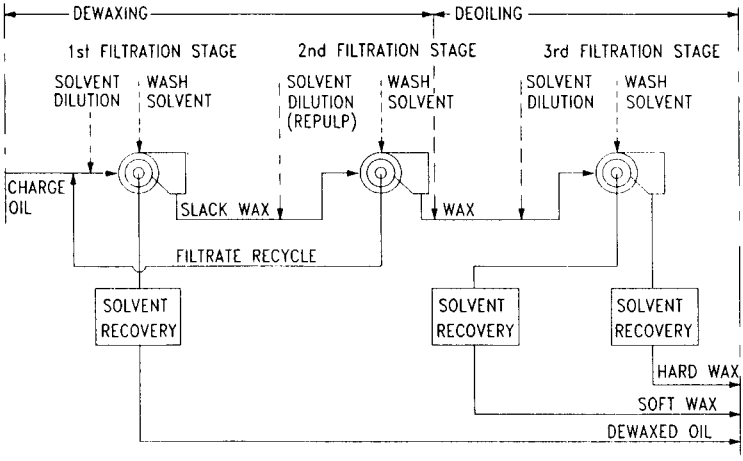

Figure 7.5 Process flow diagram of an integrated solvent dewaxing/deoiling unit. (Reprinted from Ref. [5], p. 369.)

diluted and mixed with warm solvent and filtered at a temperature which provides a hard wax of the desired melting point; the solvent recovered from the low oil content hard wax, soft wax and dewaxed oil by distillation is recycled in the process. The warm-up deoiling procedure is more cost-effective than the recrystallization procedure for manufacture of low oil content waxes because capital and energy requirements are lower; the hard wax is not melted and recrystallized before filtration. In addition, scraped-surface exchangers and chillers are not required. The warm-up deoiling procedure was used in parallel with ketone dewaxing by one refiner in the late 1940s and early 1950s and has been used in the Di/Me dewaxing process since about 1954. However, it did not become widely used until the advent of the Dilchill Process and refiners' concern for the high cost of energy.

C. The Wax Recrystallization Processes [2,9,10,19,20,21]

These processes also called wax fractionation processes were developed as a replacement for the wax sweating process and can be used to fractionate or deoil all types of waxes.

The process flow for wax fractionation depends on the operational (series or parallel) method used. When the recrystallization is used in conjunction (series) with dewaxing, the flow is similar to that depicted in Figure 7.5 with an additional heater and chiller installed between the second and third filtration stages.

The filtration of the wax in the third stage is conducted at a higher temperature than that used in the first or second dewaxing and repulp filtrations; the

temperature used is selected to adjust wax melting point and penetration. These processes can be operated in series with the solvent dewaxing unit or in blocked operation of the slack wax as the feed to the solvent dewaxing unit or a wax deoiling unit of similar design which uses double or incremental dilution and single or two stage filtration. Recrystallization processes are licensed by Texaco and Unocal.

D. The Spray Deoiling Process [22,23]

The spray deoiling process is a development of Edeleanu which can be used to deoil macrocrystalline wax containing up to 15 weight percent oil. This process like the sweating process is not suitable for the deoiling of malcrystalline wax. A simplified flow diagram for this process is shown in Figure 7.6 and 7.7. Molten slack wax is atomized under pressure into the top of a tower. The finely dispersed droplets of wax fall through a rising stream of air which is cooled to slightly below ambient conditions. The solidified wax settles to the bottom of the tower as a dry powder. Any oil which adheres to the wax is removed by a counter current flow of -40 to 60°F solvent (dichloromethane) in two or more mixer settlers and separated into two layers in a settling tank. The wax leaving the last settler is centrifuged and washed with fresh solvent. The solvent is recovered from the hard and soft wax by flash vaporization and the dry solvent is recycled in the process.

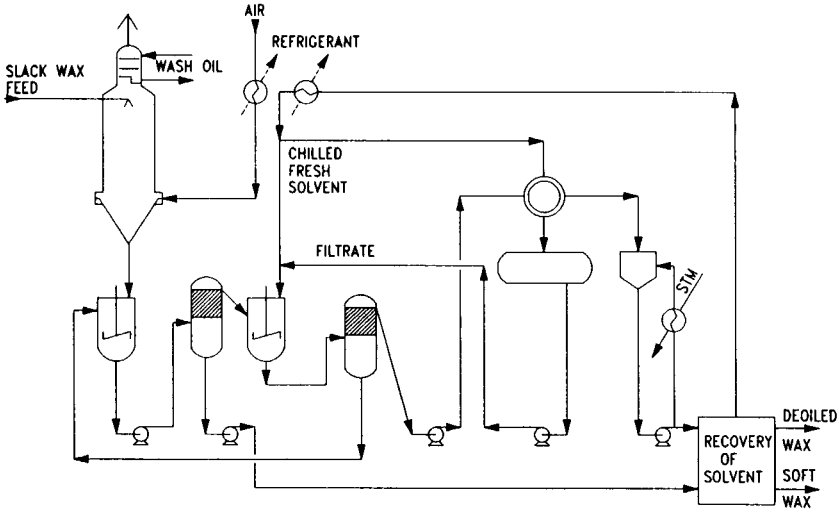

Figure 7.6 Spray deoiling process crystallizing and repulp section. (Reprinted from Ref. [22], p. 7 by courtesy of Edeleanu.)

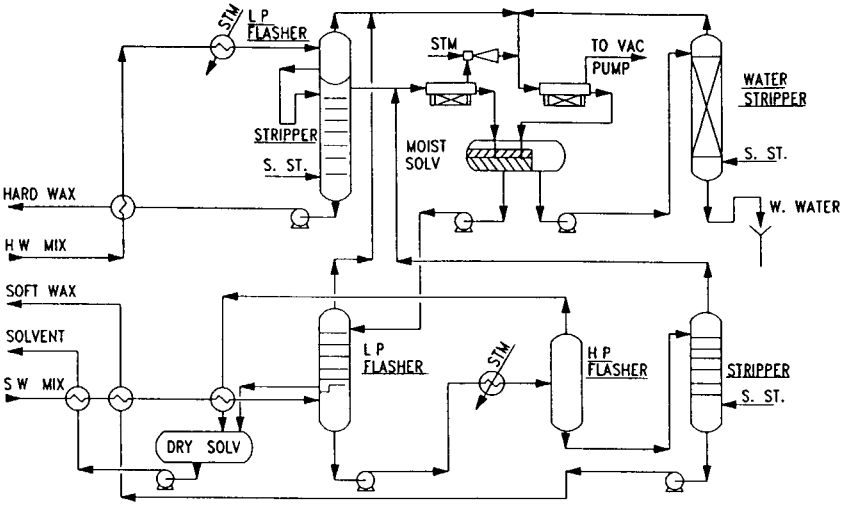

Figure 7.7 Spray deoiling process solvent recovery section. (Reprinted from Ref. [22], p. 8 by courtesy of Edeleanu.)

IV. PROCESS VARIABLES

Table 7.2 lists the process variables which have a significant effect on the operation and economics of the dewaxing process.

A. Quality of the Feedstock

The quality of the feedstock to a solvent dewaxing unit will influence the method in which the unit is operated and the throughput for a specific unit. A listing of the more important feedstock parameters is shown in Table 7.3.

The viscosity and wax content of the feed are the key determinants of solvent dilution ratio and thus have a profound effect on refrigeration requirements, filtration rates and size of the solvent recovery facilities. The boiling range and type of wax are related and can significantly affect filtration rates. The wax content is generally related to crude source and will affect the filtration rates as well as dewaxed oil yield. Prior processing, the storage and the blending of feedstocks can change the boiling range, wax content, and type of wax which in turn can have an effect on filtration rates.

The filtration rates of the dewaxing and deoiling processes decrease with 1) an increase in viscosity of the feedstock and 2) a decrease in pour point of the oil being manufactured. Filtration rate is lowest for the most viscous feedstock which also require the highest solvent dilution. The filtration rate shows a dramatic decrease between 300 to 500 SUS; the higher boiling end point oils.

Table 7.2 Dewaxing Process Variables

Process variable
Feedstock—crude source, viscosity, boiling range
Solvent and solvent composition
Crystallization—dilution and chilling procedure
Filtration—filter operation and number of stages
Solvent recovery—type and number of stages
Process variables affect
Production rates of wax and dewaxed oil
Yields of wax and dewaxed oil
Pour point of dewaxed oils
Oil content and melting point of waxes
Investment costs and operating costs

In such high boiling oils, waxy hydrocarbons occur as microcrystalline or malcrystalline wax rather than macrocrystalline or paraffin wax. Microcrystalline waxes filter more slowly. The exact temperature at which this occurs is not well defined but it is generally found that small amounts of waxes with boiling points above about 1000°F are microcrystalline in nature.

Methods which increase feedstock end point include 1) poor fractionation, and 2) maximizing distillate grade and adjusting feedstock viscosity by blending a heavy oil with a light oil.

High wax content feedstocks will filter poorly and may require the use of high solvent dilutions. However, it should be noted that a wax manufacturer that does not wish to manufacture lubricating oils will find high wax content feedstocks highly desirable. Data in Figure 7.8 show how dewaxed oil yield varies with wax content as related to crude source [24]. The data in Figure 7.8 show that dewaxed oil yield is considerably higher (wax content is lower) for a West Texas distillate as compared to a distillate from Minas Crude. The data also show that the amount of wax or dewaxed oil varies with pour point of the product oil. Filtration rates would also be lower when dewaxing high wax content feedstocks because the wax cake would be thicker resulting in a high resistance to flow of the solution of dewaxed oil and solvent (filtrate mix) and wash solvent.

Table 7.3 Feedstock Parameters

Viscosity	Product pour
Boiling range	Wax type
Wax content	Crude source
Prior processing	Handling-mixing

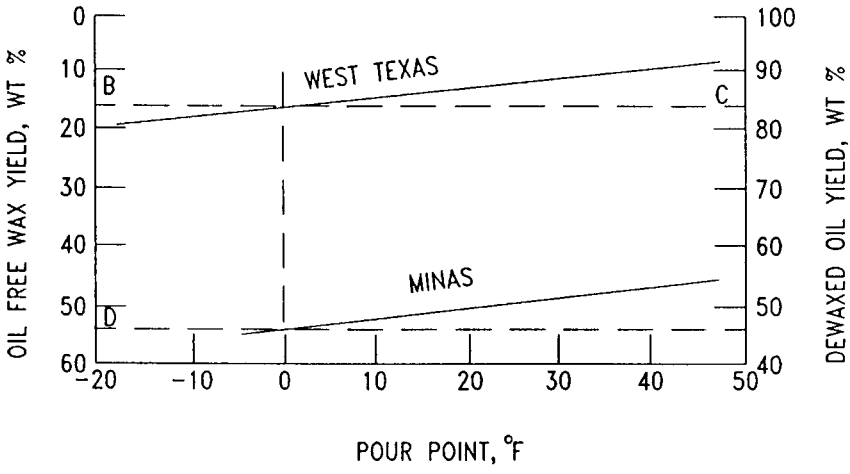

Figure 7.8 Ultimate dewaxed oil yield for a light neutral raffinate. (Reprinted from Ref. [24] by courtesy of Texaco, Inc.)

B. Prior Processing

Prior processing such as propane deasphalting, solvent extraction and hydrocracking remove asphaltic and aromatic materials and increase the wax content of the feedstocks to dewaxing. The net effect of prior processing on filtration rate can be beneficial or detrimental and is highly dependent on crude source. For example, rates of filtration will generally improve on removal of asphaltic materials and decrease with an increase in wax content. However, it should be noted that very low wax content feeds will filter poorly and require the recycle of wax to optimize filtration rate and the use of trace quantities of filter aids will sometimes improve filtration rate. Refining will decrease or eliminate the need for use of wax recycle with some low wax content feedstocks. Some hydrocracked oils will also generally filter more poorly than the solvent extracted oils prepared from the same feedstock. The reason for this is related to an increase in the iso-paraffin and cycloparaffin content of the waxes present in the severely hydrocracked lubricant base oils. It has also been noted that hydrocracked oils which have been solvent extracted filter better than the severely hydrocracked oils. Figure 7.9 shows how refining severity can affect wax content of the feedstock.

C. Crystallization Method

The crystallization method has a significant effect on the type and filterability of the wax crystals formed.

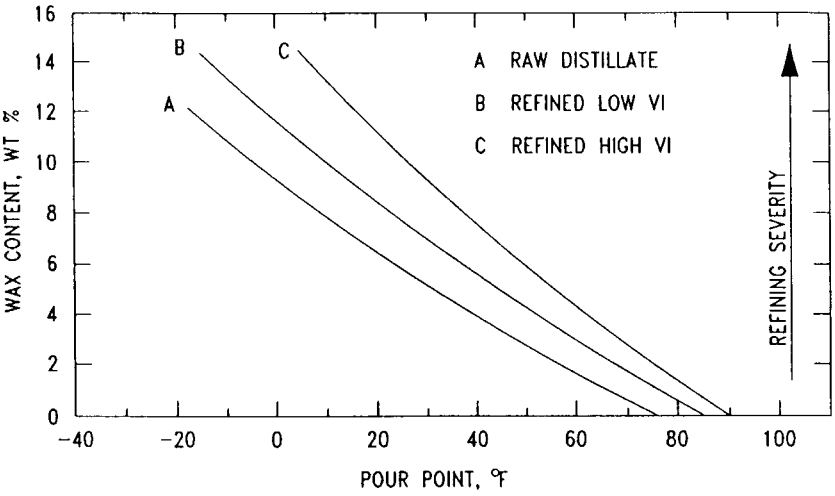

Figure 7.9 Wax content of a raw and refined distillate.

Some of the more important parameters affecting the operation of a solvent dewaxing unit are listed below and discussed in the sections that follow.

Feedstock preparation	Solvent composition
Dilution type	Dilution size
Chilling rate	Chilling method

In the crystallization–filtration flow scheme shown in Figure 7.10 the waxy feedstock is heated to 10–15°F above the cloud point of the oil and diluted with solvent while chilling at a controlled rate in double-pipe scraped-surface

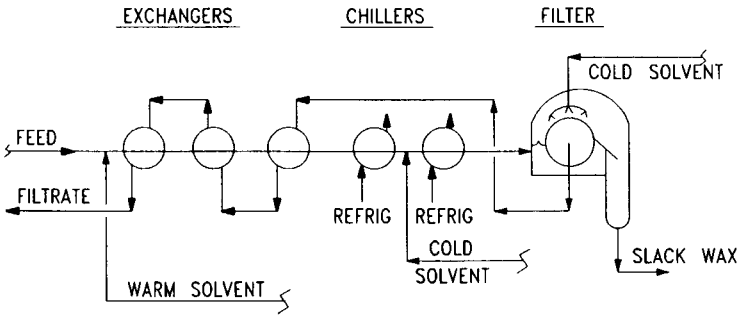

Figure 7.10 Double dilution–single stage filtration procedure. (Reprinted from Ref. [20] by courtesy of Texaco, Inc.)

exchangers and chillers. About 60 percent of the chilling is obtained by heat exchange between the feedstock and solvent with the cold filtrate from filtration in the annulus of the double pipe exchangers. In the Dilchill process, the scraped surface exchangers are replaced with a crystallizer and wax crystallization is conducted using cold solvent. The remainder of the refrigeration required for chilling is obtained by indirect heat exchange with a refrigerant in the annulus of the double pipe chillers. The slurry of wax, oil and solvent at a temperature of 5 to 20°F below the desired pour point is the feed to the dewaxing unit filters.

Scraped-surface exchangers and chillers of 12 inches in inner pipe diameter are being used in new dewaxing units and are replacing the smaller diameter inner pipe exchangers and chillers. Advantages for use of the larger diameter equipment include 1) a lower pressure drop, 2) the need for fewer crystallization trains, 3) less plugging of the scrapped surface equipment, and 4) lower maintenance costs. A schematic flow diagram for the double-pipe scraped-surface equipment is shown in Figure 7.11

D. Feedstock Preparation

The feedstock entering the process must be heated to ensure that the wax is in complete solution. Although most units have feed preheaters, it has often been found that even though a heavy feedstock has been heated to the desired temperature and is bright and clear the expected filtration rates are not obtained. On the other hand the same feedstock which has been held in tankage at the desired temperature will filter very well. This suggests that the residence time at the desired temperature is very important and that this needed residence time

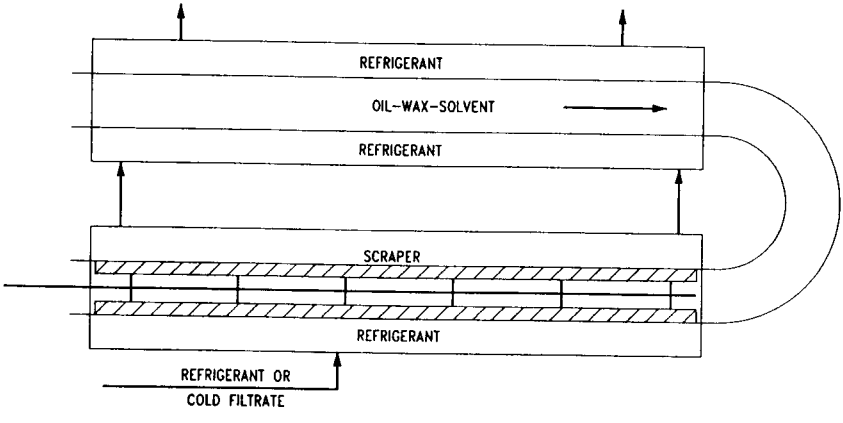

Figure 7.11 Double-pipe scraped-surface exchangers and chillers.

is not available between the preheater and chilling section of the dewaxing unit. The feedstock should not contain free water because this results in an imbalance in the solubility of the oil in the dilution solvent and requires excessive use of refrigeration to remove the water as ice and additional energy to remove the water as steam in the solvent recovery section.

E. Solvent and Solvent Composition

The characteristics of an ideal dewaxing solvent include the following:

Low solvent power for wax	Non-corrosive to conventional metals
High solvent power for oil	Easily recoverable by vaporization
Low freeze point	Adaptable to all feedstocks
Low viscosity	Low dewaxing differential
Low in cost	Good chemical stability
Non-toxic	Good thermal stability

Although no single solvent meets the above criteria, mixtures of ketones and aromatic solvents most nearly meet these requirements. The Texaco Solvent Dewaxing Process originally used acetone as the wax antisolvent and benzene as the oil solvent (the A–B Process). The Texaco Solvent Dewaxing Process is now most frequently practiced using a mixture of MEK as the wax antisolvent and toluene as the oil solvent (the MEK Process). Toluene replaced benzene as the oil solvent because toluene is less toxic, has a lower freezing point and provides better filtration rates. MEK has replaced acetone as the wax antisolvent because MEK's higher boiling point minimizes solvent losses. Methylisobutylketone (MIBK) alone and in combination with MEK is also used in some dewaxing and deoiling units as are mixtures of various other solvents such as methylene chloride and dichloroethane.

Use of neat toluene as a dewaxing solvent results in a high dewaxing differential (the difference between the pour point of the oil and filtration temperature), small wax crystals and low filtration rates. Use of neat MEK as the dewaxing solvent gives low dewaxing differentials and high filtration rates, provided the mixture is not in the oil separation region. Since oil separation occurs with most stocks when using neat MEK, a mixture of MEK and toluene is used in order to obtain good filtration rates while minimizing energy (refrigeration) requirements. Although the discussion presented below is specific to the use of MEK and toluene as dewaxing solvents, it should be noted that the basic principles apply to mixtures of other solvents. The solvent composition used in a solvent dewaxing process is dependent on the factors listed as follows.

Feedstocks to be dewaxed	Viscosity of the feedstocks
Pour point of product oil	Dilution ratio
Crude source of the feedstocks	

1. Determination of Solvent Composition [4,5]

In order to optimize the dewaxing properties of a mixture of two or more solvents the solvent composition to be used must be determined using a miscibility diagram. When using the Texaco method, the miscibility of the feedstock with mixtures of the solvents at the solvent dilution to be used is determined by preparing mixtures of the particular dewaxed feed (filtrate) of desired pour point and solvents of different composition. The cloud point of the solution of solvent, oil and wax on cooling is determined and plotted as shown in Figure 7.12 [5].

The difference between the pour point, T_1, of the filtrate and the filtration temperature, T_2, is the dewaxing differential. The dewaxing differential is an important factor in solvent dewaxing and is a function of the solvent composition used and the solubility of the wax in the feedstock. The dewaxing differential will decrease as MEK concentration is increased at constant dilution ratio and it will usually increase as dilution ratio is increased. The oil and wax separation lines intersect at the maximum MEK concentration which can be used to dewax the feedstock from which the dewaxed oil was made. Use of MEK concentrations lower than this will increase the dewaxing differential and decrease the filtration rate. Use of MEK concentrations above the maximum, to the right of line a–b in Figure 7.12, will result in a decrease in filtration rate due to the high viscosity of the oil phase, high oil content wax and low dewaxed oil yield. Dewaxing is therefore conducted at as high an MEK content as possible which does not result in oil separation. It should be noted that the miscibility for each feedstock is dependent on feedstock viscosity and composition.

The same phenomenon is obtained with all solvent dewaxing processes using mixtures of two solvents such as acetone/benzene, MEK/MIBK,

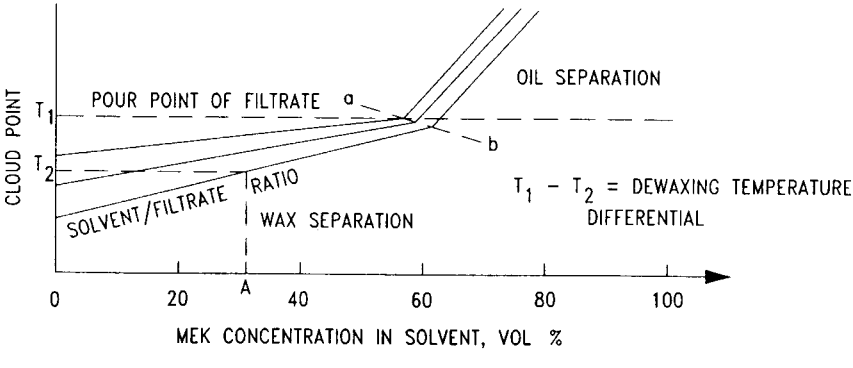

Figure 7.12 Miscibility diagram of filtrate in toluene/MEK mixtures. (Reprinted from Ref. [5], p. 355.)

acetone/toluene, dichloroethane/methylenechloride, etc. Dewaxing differentials typically range from 5 to 15°F for the ketone and Di/Me processes and 25 to 40°F in the propane dewaxing process [5].

2. Effect of Dilution Ratio on Solvent Composition

Increasing the dilution ratio will increase the dewaxing differential. This change in dewaxing differential can be seen by moving along line a–b in Figure 7.12. The higher dewaxing differential will in turn increase the refrigeration requirements and size of the refrigeration unit. However, it should be noted that selecting dilution ratios which are either too low or too high can have a dramatic effect on the economics of the process.

An alternate method for determining the optimum solvent composition to be used consists of conducting a series of laboratory batch dewaxings using a feedstock at a fixed dilution ratio with solvents of different MEK content. The composition of the filtrates is then plotted as shown in Figure 7.13 [4]. The data show that the oil content of the filtrate mix decreases as MEK content is

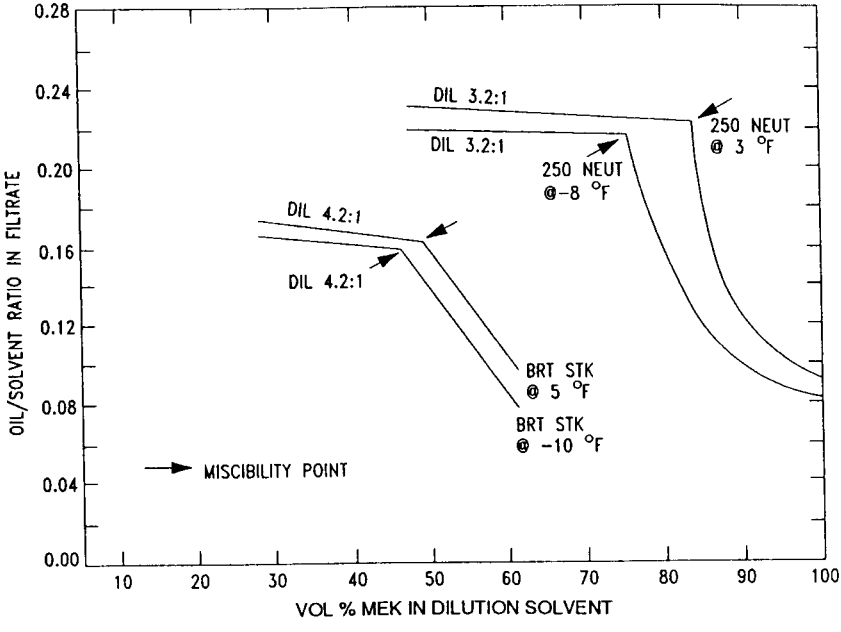

Figure 7.13 MEK–toluene miscibility diagram. (Reprinted by permission of John Wiley & Sons, Inc. from S. Marple, Jr. and L. J. Landry, "Modern Dewaxing Technology," *Advances in Petroleum Chemistry and Refining*, Vol. 24, p. 213, copyright 1965 by John Wiley & Sons, Inc.)

increased to the miscibility point. Increasing the MEK content above this point results in a rapid decrease in oil content of the filtrate. These data also show that if an oil is dewaxed to a lower pour point (using the same dilution ratio) the MEK concentration must be decreased if one is operating at the miscibility point. The rapid decrease in oil content at MEK concentrations above the miscibility point causes oil to separate which will reduce dewaxed oil yield and result in high oil content waxes.

3. Effect of Solvent Composition on Dewaxing Differential

Figure 7.14 presents additional information on the effect of solvent composition on the dewaxing differential for a 250 neutral [25]. These data show that the MEK concentration of the dewaxing solvent can have a significant effect on the dewaxing differential which can have a profound effect on the refrigeration requirements of the process. It is also interesting to note that neat MEK could be used to solvent dewax this feedstock.

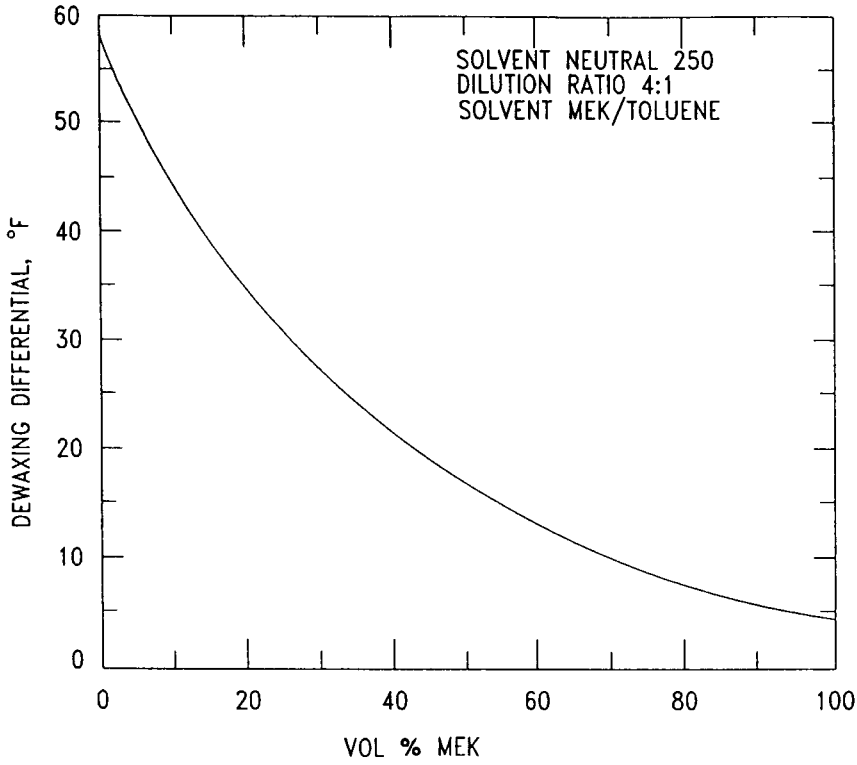

Figure 7.14 Effect of solvent composition on dewaxing differential. (Reprinted by permission from *Petroleum Refiner*, March, 1948, Gulf Publishing Co.

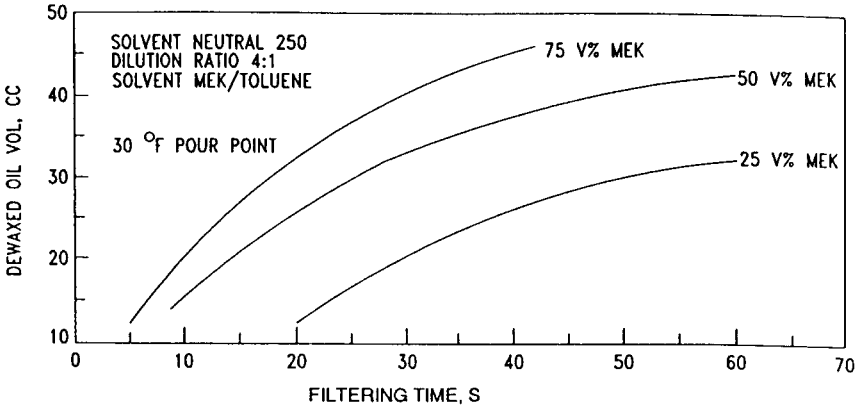

Figure 7.15 Effect of solvent composition on filtration rate. (Reprinted by permission from *Petroleum Refiner*, March, 1948, Gulf Publishing Co.

4. Effect of Solvent Composition on Filtration Rate

The effect of solvent composition on laboratory filtration rate for a 250 neutral is shown in Figure 7.15 [25]. These data show that filtration rate decreases with a decrease in MEK content. Decreasing MEK content will also result in the need for use of a lower filtration temperature which will increase the refrigeration requirements; this was previously discussed.

F. Dilution and Chilling Rate

The size and type of dilution as well as the viscosity of the solution of oil and solvent and liquid solids ratio of the filter feed mixture are important variables which have a profound effect on the filtration characteristics of each feedstock. Once the solvent is selected it is therefore important to consider these items because they will have an effect on wax crystallization, the filtration rate and the temperature at which oil and wax separation (miscibility point) occurs. High dilution ratios are used with high viscosity stocks as compared to low viscosity stocks to obtain good filtration rates.

1. Effect of Dilution Ratio on Filtration Rate

Figure 7.16 depicts how the filtration rate of a feedstock varies with dilution ratio. These data show that the filtration rate increases as dilution ratio is increased; reaches a maximum and then decreases with further increases in dilution ratio. It should also be noted that this optimum depends on the feedstock viscosity and composition, solvent and solvent composition, and product pour point. This means that addition of more than the optimum amount of solvent may not be cost-effective. Oil content of the wax will however be

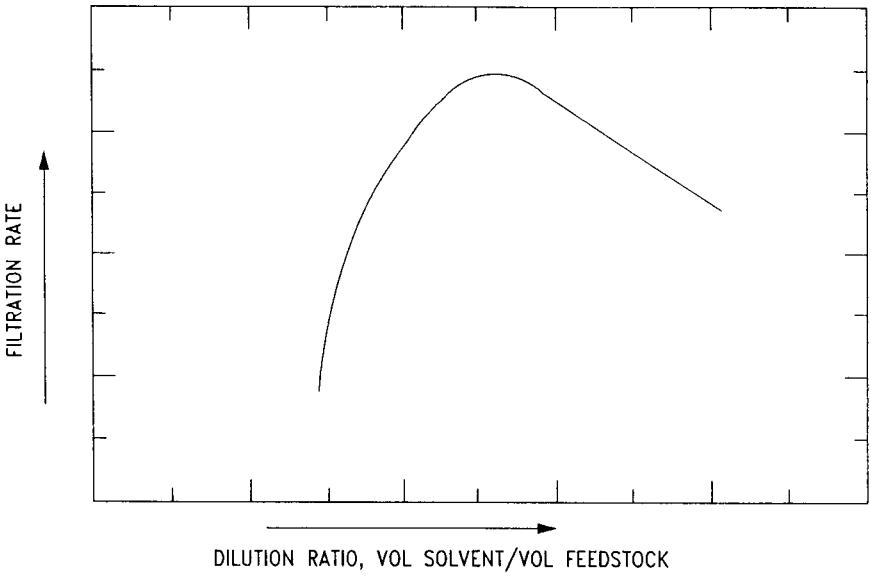

Figure 7.16 Effect of dilution ratio on filtration rate.

reduced on increasing dilution ratio because of the higher solvent–oil ratio of the solution remaining in the wax cake. It should also be noted that operation at less than the optimum filtration rate may be more cost-effective if the dewaxing unit is either refrigeration- or solvent recovery-limited and excess filter capacity is available. Conversely if the unit is not solvent- nor refrigeration-limited a higher yield of dewaxed oil and wax of lower oil content can be produced by operating at dilution ratios above the optimum for filtration when excess filtration capacity is available.

Reeves [26] used the Pouiselle equation to derive a calculational procedure for determining the optimum dilution for filtration based on the use of filtrate composition and viscosity. Readers interested in this technique for determining the optimum dilution ratio should consult this work and the summary reported by Scholten [19].

2. Effect of Dilution Ratio on Viscosity and Liquid–Solids Ratio

Additional considerations in the selection of the dilution ratio to be used are the viscosity of the solution, pressure drop in the crystallization section, and the ratio of liquid (solvent + oil) to solids (wax) at the filter. A high viscosity or low liquid–solids ratio may result in high pressure drop and poor filtration as well as high oil content wax. Use of high dilution ratios can lead to low viscosity which will result in poor filtration rates and excessive use of energy for refrigeration and solvent recovery.

3. Dilution Procedures [20]

The type of solvent dilution procedure being used has a significant effect on the wax crystals which affects the filtration rate and yield of dewaxed oil. The types of dilution procedures currently in use consist of the following:

Single dilution–single stage filtration.
Double dilution–single stage filtration.
Double dilution–two stage filtration.
Multiple dilution–single stage filtration.
Incremental dilution–two stage filtration.

The double dilution–single stage filtration procedure depicted in Figure 7.10 replaced the single dilution–single stage filtration procedure and is still being used by some refiners. This procedure is more cost-effective because it provides better crystallization and better filtration rates than the single dilution procedure.

The use of the double dilution–two stage (repulp) filtration procedure shown in Figure 7.17 was introduced as a means of improving the cost-effectiveness of the MEK dewaxing process. The use of the repulp filtrate as dilution solvent reduces energy requirements and repulp filtration decreases the oil content of the wax and increases dewaxed oil production rates. Laboratory studies and commercial experience have demonstrated that a double-dilution controlled shock chilling procedure with repulp filtration is preferred for dewaxing of heavy feedstocks and that a multiple or incremental dilution procedure, shown in Figure 7.18, with repulp filtration is more cost-effective for the dewaxing of light and medium viscosity grade feedstocks. These procedures have been used by Texaco for about 30 years and have been adopted by some refiners under license from Texaco Development Corporation. The Dilchill process licensed

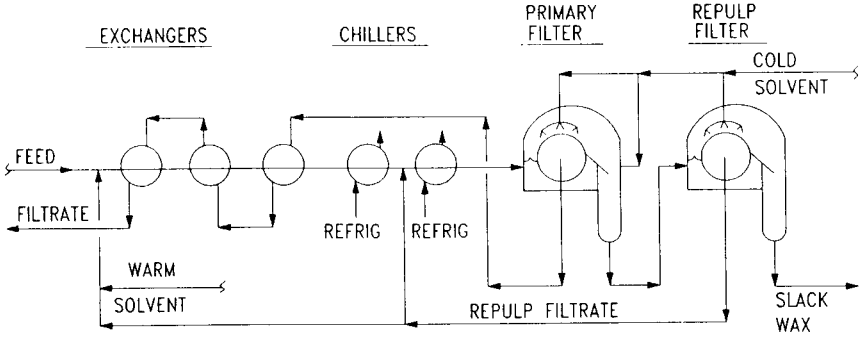

Figure 7.17 Double dilution–two stage filtration procedure. (Reprinted from Ref. [20] by courtesy of Texaco, Inc.)

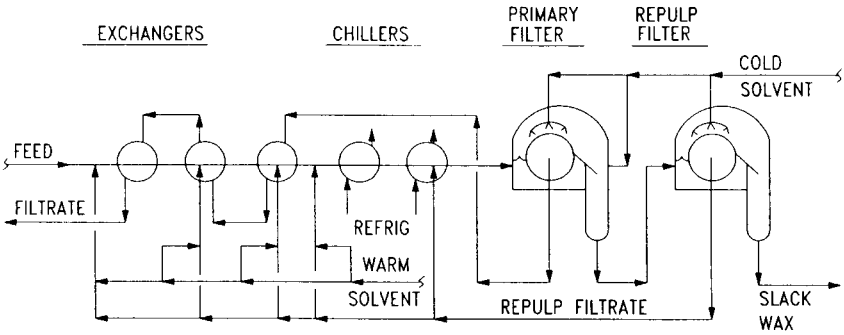

Figure 7.18 Incremental dilution–two stage filtration procedure. (Reprinted from Ref. [20] by courtesy of Texaco, Inc.)

by Exxon also uses a multiple dilution procedure in a special crystallizer followed by single or two stage filtration.

4. Effect of Dilution Ratio on Oil Content of Wax

The effect of the size of the primary dilution on oil content of the wax from a single stage filtration is shown in Figure 7.19 [25]. These data show that the

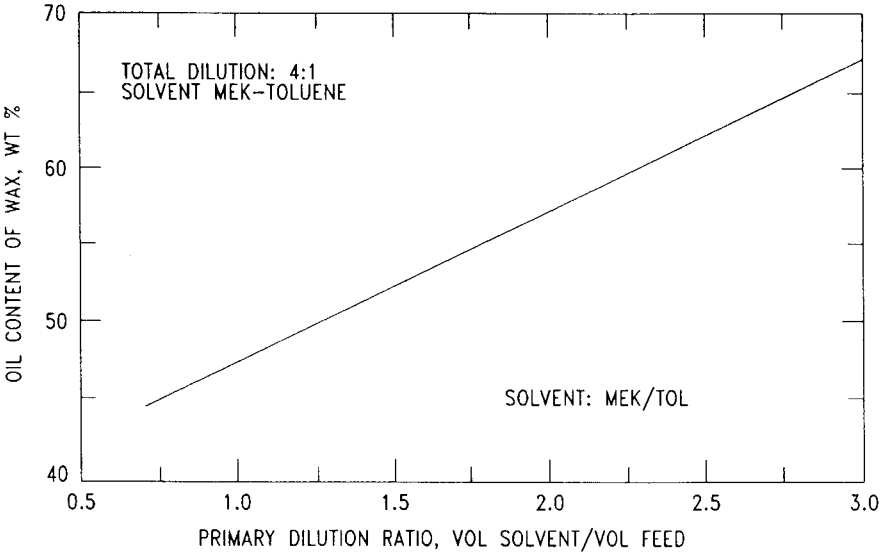

Figure 7.19 Effect of primary dilution on oil content of wax. (Reprinted by permission from *Petroleum Refiner*, March, 1948, Gulf Publishing Co.

smaller the primary dilution the lower the oil content of the wax. The lower oil content results from the fact that the wax crystals are purer when precipitated from a rich mother liquor. However, it should be noted that the minimum size of this primary dilution is limited by the design and pressure drop of the liquid–wax slurry in the double-pipe scraped-surface exchangers and chillers. It should also be noted that this procedure does not work as well as the Texaco controlled shock chill procedure with heavy feedstocks.

Table 7.4 presents a quantitative comparison for both single and double stage filtration for the double and incremental dilution procedures. These data

Table 7.4 Comparison of Dewaxing Procedures

Light neutral dewaxing with refrigeration limitations (12,000 BPOD unit)			
Number of dilutions	Two	Two	Five
Number of filtration stages	One	Two	Two
Dewaxed oil yield, volume %	81	82	85
Wax oil content, weight %	15	10	NA
Total solvent circulation, bbl/bbl	3.1	2.35	2.18
Filtration rate, gal feed/hr/sq ft	3.38	4.8	5.0
Percent increase	—	42	48
Energy consumed/bbl feed			
Electricity, kWh	1.1	0.9	0.78
150 psig steam, lbs	170	140	160
Fuel, MBtu/bbl	477	379	148
Total FOEB/Mbbl	93.1	76.3	58.4
Percent reduction	—	18	37
Heavy neutral dewaxing (5000 BPOD capacity)			
Number of dilutions	Two	Two	Shock
Number of filtration stages	One	Two	Two
Dewaxed oil yield, volume %	80	81	82
Wax oil content, weight %	17	13	NA
Total solvent circulation, bbl/bbl	5.5	4.3	3.1
Filtration rate, gal feed/hr/sq ft	2.35	3.0	3.0
Percent increase	—	28	28
Energy consumed/bbl feed			
Electricity, kWh	1.2	1.0	2.24
150 psig steam, lbs	225	180	138
Fuel, MBtu/bbl	462	365	233
Total FOEB/Mbbl	186.9	97.6	70.1
Percent reduction	—	48	62

Reprinted from Ref. [20] by courtesy of Texaco, Inc.

are from operating records before and after conversion of two different commercial units from single stage to two stage filtration [20]. These data show that unit throughput was significantly increased and energy requirements were reduced on conversion to the two stage filtration procedure. The data also show that significant energy reductions were obtained by using the incremental dilution and the controlled shock chill procedure with the light and heavy neutral feedstocks, respectively.

5. Effect of Chilling Rate [1,5]

The chilling rate used in the crystallization section can have a significant effect on the filtration rate. It has a greater effect in propane dewaxing than in ketone dewaxing. Low chilling rates provide higher filtration rates than do high chilling rates. A typical curve for a MEK dewaxing unit is depicted in Figure 7.20.

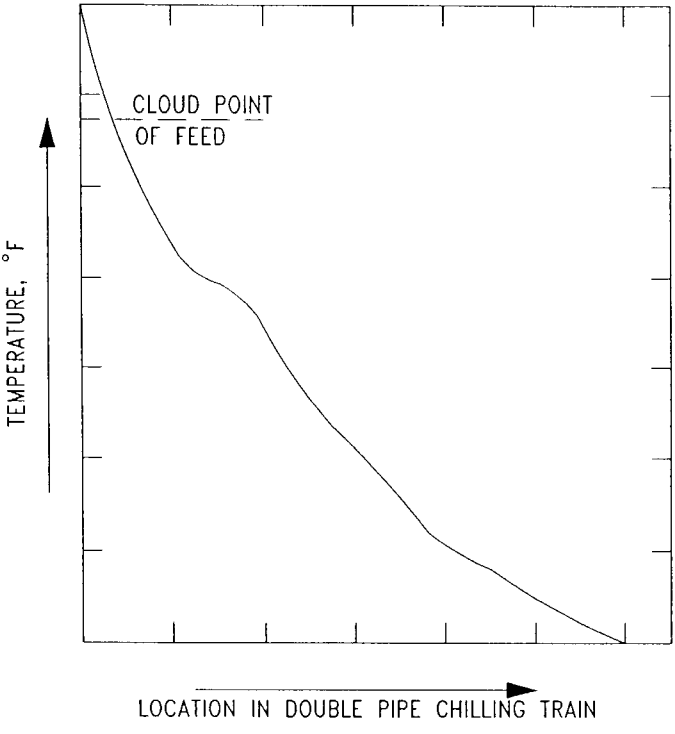

Figure 7.20 Chilling curve for ketone dewaxing. (Reprinted from Ref. [9] by courtesy of Texaco, Inc.)

G. Dewaxing Aids

The use of dewaxing aids to improve dewaxing processes are strongly promoted by vendors of these materials and some refiners have reported improved filtration rates and lower oil content waxes from use of different types of dewaxing aids. It is generally believed that dewaxing aids are beneficial in the Propane Dewaxing Process [4,5]. Dewaxing aids are probably less beneficial in the ketone dewaxing processes. Laboratory studies and commercial experience by some refiners have shown that dewaxing aids are not normally required in the ketone dewaxing processes. It appears that dewaxing aids should be used as another process (crystallization) variable, because the quantity and type of dewaxing aid used appears to vary considerably with feedstock (viscosity grade as well as crude source). It has also been found that in some cases any quantity of dewaxing aid can be detrimental or beneficial. It has also been observed that when dewaxing the same viscosity grade of oil the quantity of dewaxing aid used must sometimes be changed to obtain beneficial results. Selection and adjustment of the dilution and crystallization procedures will in most cases also eliminate the need for dewaxing aids in the ketone dewaxing processes. A listing of some of the types of materials being used as dewaxing aids and comments are provided in Table 7.5.

H. Filtration

Filtration is normally carried out in continuous rotary vacuum filters of 500 to 1250 square feet in filter area. The operation of these filters is depicted in Figure 7.21. The filter drum is totally enclosed and rotates inside the enclosure; vat. The drum surface is divided into a number of sections which are parallel to the drum axis. Each section contains drainage members consisting of an inserted grid or special wire mesh 3/8 to 3/4 inch thick. The sections are separated by strips and the filter cloth is held in place with caulking and wound with wire. Each section contains a drainage member and is connected by its

Table 7.5 Solvent Dewaxing Aids

Types of solvent dewaxing aids	
N-alkylated naphthalene polymers	Microcrystalline waxes
N-alkyl polymethacrylates	Proprietary polymers
N-alkyl polyaromatics	Aromatic extracts
Asphaltenes	Vacuum residua
Comments	
Not always effective	Feedstock sensitive
A process variable	Sometimes harmful
Quantity sensitive	Type sensitive

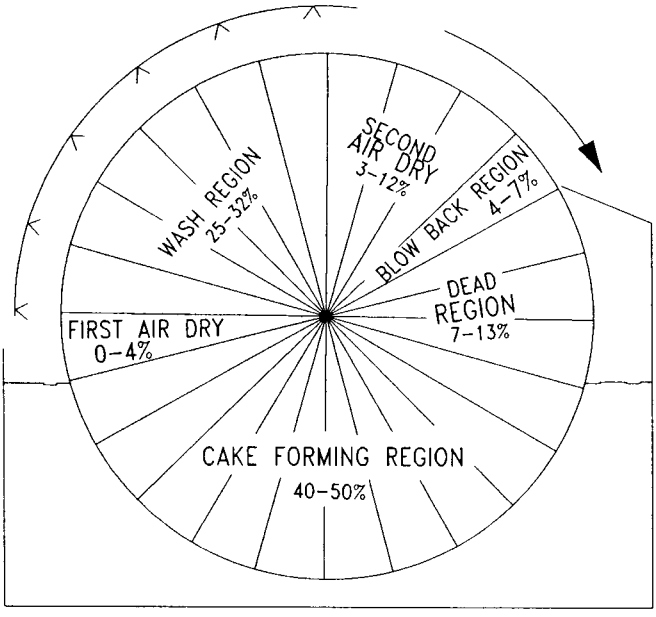

Figure 7.21 Pictorial presentation of filter cycle time.

own piping system to the rotating portion of the filter valve. As the filter rotates vacuum or an inert gas purge can be directed to the filters and filtrate can be diverted to separate receivers as desired. The piping system consists of a lead and trailing pipe to each section which permits efficient drainage of the filter sections and permits controlling the purge through one set of piping to purge the filtrate from the drainage members through the other set of piping. These pipes are also used for the reverse air blow used to discharge the cake from the filter cloth which is then directed from the drum by a deflector or scrapper blade.

The diluted-chilled mix enters the bottom of the vat and a level is maintained to provide the desired submergence of the filter drum. The filter rotates through this slurry and the filtrate (solution of oil and solvent) is removed by vacuum. As the wax cake, formed on the filter cloth emerges from the slurry, it is washed continuously by a spray of cold solvent to remove a portion of the occluded solution of oil and solvent. As the filter continues its rotation the wax cake enters the drying zone wherein vacuum pulls an inert gas through the wax cake which replaces some of the wash solvent and oil occluded in the wax cake. Following the drying of the wax cake, the cake is removed by a combination of an inert gas blow back through the filter cloth and a deflector blade located very close to the wires holding the filter cloth in place. The wax cake

then drops into scroll-type conveyers. The dilution and handling of this slurry at this point depends on (1) whether repulping is used or (2) whether repulping and/or warm-up oil deoiling or recrystallization is being used to manufacture hard wax. The filtrate and wash solvent from the primary filter are used to prechill the solvent and oil in the scraped surface exchangers and are then distilled to recover the dewaxed oil.

1. Filtration Variables

Variables which have an important effect on the filtration results include the feedstock properties and the crystallization methods discussed in the preceding sections. Additional parameters which will be described and which affect dewaxed oil filtration rates and quality as well as process economics are:

Filters	Filter cloth
Operational mode	Filter washing method
Filter speed	Filtrate recycle rate
Vacuum (pressure differential)	Wax recycle rate
Wash ratio	Cake thickness

Operation of the rotary vacuum filters is ordinarily controlled to give good filtration rates and efficient cake washing which means that cake thickness will be controlled at about 1/8 to 1/4 inches. The cake thickness can be increased by decreasing filter speed and/or increasing the pressure differential. Cake thickness can be reduced by increasing filter speed and/or using a lower pressure differential in the cake forming region. Wax cakes which are too thick have the following disadvantages:

Low filtration rates.
Low dewaxed oil yield.
High oil content wax.
Poor washing of the wax cake.
Dropping off of the wax cake.

Methods used to thin thick wax cakes and improve filtration rates are:

Increase the filter speed.
Recycle filtrate to the filter feed.
Block out a portion of the cake forming zone.
Use a lower pressure drop in the filtration zone.

Use of a filtrate recycle or blocking out a portion of the cake forming region results in a thinner wax cake and a higher yield of dewaxed oil; however the dewaxed oil production rate will decrease.

Wax cakes below about 1/8 inch in thickness have the following disadvantages:

Faster blinding of the filter cloth.
Wax discharges poorly or fails to blow off.
Wash solvent is not efficiently used.

These disadvantages may be overcome by increasing cake thickness using the methods listed as follows.

Decrease the filter speed.
Recycle a portion of the wax cake to the filter feed.
Recycle a portion of the wax to the unit feedstock.
Increase the pressure differential in the cake forming zone.
Increase size of the cake forming zone, if possible

Recycle of wax to the unit feed to increase cake thickness is frequently used when dewaxing feedstocks which are low in wax content.

2. Filter Cloth

The early filter cloths were made of cotton canvas. Because cotton cloths are not as durable as synthetic cloths they are short-lived and have been largely replaced with single or double layer synthetic cloths. The synthetic cloths are more durable, require fewer repairs and improve on-stream time thus improving the economics of the process. Cotton canvas is still used in some units for the dewaxing of high viscosity feedstocks to eliminate the possible formation of wax haze. Since the wax haze is not observed in laboratory filtrations using the more common synthetic filter cloths, it is believed that the wax haze problems observed in commercial operations are related to poor filter maintenance and mechanical leakage in commercial dewaxing units.

The operational mode or method of filtration has a significant effect on the wax crystals which affects the filtration rate and yield of dewaxed oil. The types of operational modes which also involve the method of crystallization currently in use consist of the following:

Double dilution–single stage filtration; Figure 7.10.
Double dilution–two stage filtration; Figure 7.17.
Incremental dilution–two stage filtration; Figure 7.18.

The effect of the dilution method and crystallization method were described earlier.

The use of the two stage (repulp) filtration procedure which uses the repulp filtrate as dilution solvent was introduced as a means of improving the cost effectiveness of the Texaco MEK Dewaxing Process by increasing filtration rates and reducing filtration requirements. A summary of the benefits derived from use of repulp filtrate as dilution at constant feed rate follows:

Reduces refrigeration requirements.
Reduces energy for solvent recovery.
Decreases oil content of the wax.
Increases dewaxed oil production.
Decreases required filtration area.
Increases filtration rates.

3. Effect of Wash Ratio

The resistance of the wax cake and filter cloth influence the amount of wash solvent which can be used to deoil the wax cake. The resistance of the wax cake is affected by the dilution and chilling procedures used and the thickness of the wax cake. The resistance of the filter cloth includes the resistance of the neat cloth as well as the resistance resulting from blinding of the filter cloth; this resistance is time- and feedstock-dependent. The methods for decreasing wax cake thickness and improving the washing efficiency were discussed above. However, it should be noted that there is a trade off between washing efficiency and dewaxed oil production.

Based on material balances and a model for flow in capillaries, Butler and Tiedje [27] identified two washing sequences. In the initial sequence, the wash solvent displaces the filtrate in the capillaries and the filtrate was found to be the same composition as the filtrate from the filter feed. After breakthrough of this filtrate, the filtrate leaving the filter is a mix of original filtrate and wash solvent. Although the calculational procedure is not precise, it is useful in analyzing filter operations.

Since the flow of the wash solvent in the capillaries is laminar, wash solvent breakthrough occurs when the volume of wash solvent is about 0.5 of the filtrate contained in the original wax cake. Subsequent wash solvent is not as effective and experimental data are required to determine the effect of wash ratio. Difficulties in predicting the effectiveness of wash ratio on the deoiling of filter cakes arise from the fact that the wax cake is compressible and the porosity of the cake decreases with increased washing. In addition, the blinding of the filter cloth with time also results in an increase in cloth resistance as does changes in the dilution–chilling procedure and quality of the feedstock with time. Readers interested in the experimental and calculational techniques should consult the work of Butler and Tiedje [27] and the summary provided by Scholten [19].

4. Effect of Filter Speed on Filtration

Increasing filter speed will usually provide a higher volume of filtrate for a given period of time. However, it should be noted that operation at excessively high speeds may result in an increase in the oil content of the wax and that excessively thin wax cakes will blind the filter and reduce unit capacity.

Reeves [28] and Mondria [29,30] used the basic filtration equation based on Pouiseuille's law to relate the effect of filter speed on filtration rate and quality

of the wax cake. Readers interested in these techniques should consult these works and the summary reported by Scholten [19].

5. Effect of Vacuum on Filtration

Increasing the vacuum (pressure differential) used in filtration increases the cake thickness, filtration rate, dewaxed oil yield and wash ratio. The oil content of the wax may either increase or decrease depending on the wax content of the feed.

6. Fouling of Filter Cloths

Filter cloth resistance to filtration is small for clean cloth. However, fouling of the filter cloth increases with time on stream until the resistance becomes so high that the filter is taken off line and hot washed to maintain dewaxed oil production. Materials which cause fouling are 1) wax crystals, 2) ice and 3) insoluble impurities which may enter the process via contamination of the feedstocks or solvents. The need for washing of the filters to remove these impurities is evidenced by 1) a reduction in filtration rate, 2) excess run-off of the wash solvent, 3) the oily appearance of the wax cake, 4) a reduction in dewaxed oil yield (increased oil content of the wax) and 5) wax cakes of uneven thickness (lumps and bare spots on the filter media).

7. Hot Washing Procedures

Although the frequency with which a filter needs to be hot washed to remove the fouling materials and improve filtration rate varies considerably, the hot washing frequency used most often is once every eight hours. Hot washing of the filter is usually done using one of the two methods listed below.

Filter hot spray washing procedure:

1. Remove the filter from service.
2. Drain the filter.
3. Spray the filter with hot solvent.
4. Drain hot solvent from the filter.
5. Spray the filter with cold solvent.
6. Return the filter to service.

Filter hot backwashing procedure:

1. Remove the filter from service.
2. Drain the filter.
3. Backwash the filter with hot solvent.
4. Drain hot solvent from the filter.
5. Spray the filter with cold solvent.
6. Return the filter to service.

The filter hot backwashing procedure is preferred because it will remove insoluble impurities on the filter cloth as well as wax, ice and insoluble accumula-

tions between the filter drum and cloth which are not removed by the spray washing method.

8. Cold Backwashing Procedure

The most recent development in filter washing involves use of a cold backwashing technique which uses a cold solvent or filtrate in place of the hot spray washing technique. The use of this method, depicted in Figure 7.22, eliminates the need to remove the filter from service; it is normally done on an intermittent basis and increases on stream time which leads to increased dewaxed oil production [20]. Although this flow scheme shows the use of repulp filtrate as the backwash solvent, cold solvent or primary filtrate can also be used. Data collected during the preliminary trials using the cold backwashing procedure are summarized in Table 7.6 [20].

V. SOLVENT RECOVERY

A. Multiple Effect Evaporation [20]

The solvent based processes used for the manufacture of lube oils are energy intensive because large volumes of solvent must be recovered by flash distillation for recycle in the process. The number of stages used for evaporation of

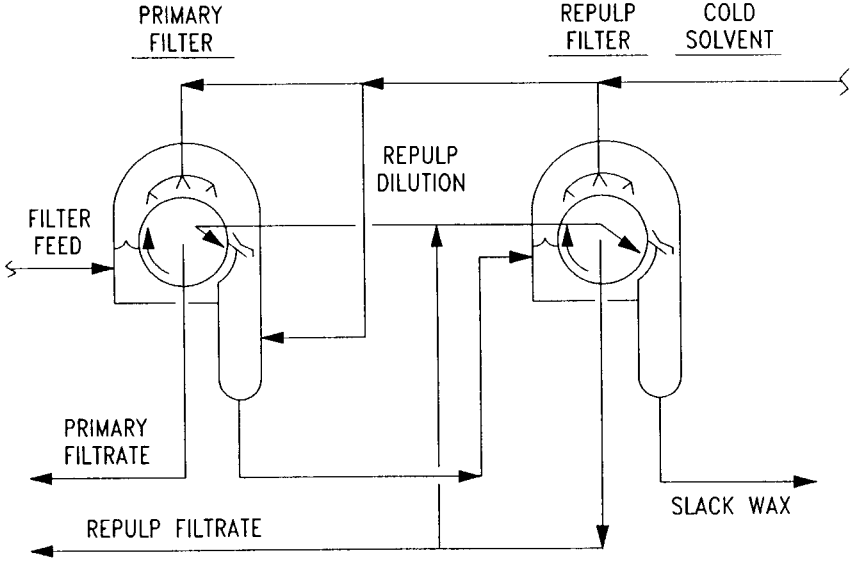

Figure 7.22 Cold backwashing of dewaxing filter. (Reprinted from Ref. [20] by courtesy of Texaco, Inc.)

Table 7.6 Comparison of Cold and Hot Backwashing of Filters

	Filter A	Filter B	Change, %
Test period, hours	24	24	
Number of hot washes	3	1	−67
Number of cold washes	0	6	—
Filter operation time			
Off line, minutes	30	10	—
On line, percent	97.9	99.3	+1.4
Filtration rate, percent			
After hot washing	100	100	
Before hot washing	92	98	+6.5
Average	95	99	+4.2
Starting filter rate, BPH	83	83	

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the solvent has a significant effect on the energy costs for these processes and as many as five evaporation stages were used in some early liquid sulfur dioxide extraction units located in Europe. Since energy was cheap, most of the units built between about 1950 and 1975 used double-effect evaporation and a few refiners used single-effect evaporation. Since the cost of energy increased considerably during the 1970s, most new units built since about 1980 have been designed with (and older units converted to) triple-effect evaporation to reduce the cost of energy consumed in these processes. A comparison of the effect of the number of stages on multistage evaporation is presented in Table 7.7.

Simplified flow diagrams for the double-effect and triple-effect evaporation schemes are provided in Figures 5.31 and 5.32 of Chapter 5. Table 7.8 presents data comparing the energy requirements for three solvent dewaxing–wax fractionation units using different numbers of evaporation stages [8].

Energy reductions for use of multiple-effect versus single-effect evaporation are lower than those calculated from theoretical considerations because part of the energy was not recovered from condensing vapors.

B. Inert Gas Stripping [20,26]

Another method for reducing the energy requirements in solvent dewaxing, depicted in Figure 5.33, involves using inert gas in place of steam for stripping the last traces of solvent from the dewaxed oil and waxes. A summary of the benefits to be realized from the use of inert gas stripping is provided below.

Table 7.7 Theoretical Comparison of Evaporation Stages

Single effect
1. Solvent is vaporized at one pressure level.
2. Energy is wasted in condensation; it is not recovered.

Double effect
1. Solvent is vaporized at two pressure levels.
2. One-half of the solvent is vaporized at each pressure level.
3. Condensing vapors are used to operate the first evaporator.
4. Energy requirements are reduced by 45 to 50 percent.

Triple effect
1. Solvent is vaporized at three pressure levels.
2. One-third of the solvent is removed at each pressure level.
3. Condensing vapors are used to operate the first two stages.
4. Energy requirements are reduced by an additional 30–33 percent.
5. Energy requirements are 30 to 33 percent of single effect.

Benefits from Use of Inert Gas Stripping

Energy requirements reduced	Dilution ratios reduced
Dewaxed oil yield increased	Solvent losses reduced
Dewaxing differential decreased	Maintenance costs reduced

The energy savings realized by one refiner on conversion to inert gas stripping are summarized in Table 7.9 [31].

The data reported in Table 7.9 show that the savings realized from the use of inert gas stripping are significant and show a nine month payout for the investment. The energy savings alone are significant and show a payout of about 14 months. This technology is available under license from Nofsinger or Texaco Development Corporation.

Table 7.8 Energy Requirements for Solvent Recovery Ketone Dewaxing

Case number	I	II	III
Number of dilutions	1 or 2	Multiple	Multiple
Number of filtration stages	1	2	2
Number of evaporation stages	1	2	3
Energy requirements			
Bbl fuel oil/bbl feedstock	10	7	5
Percent of case I	100	70	50
Percent of case II	143	100	71

Reprinted from Ref. [8] by courtesy of Texaco, Inc.

Table 7.9 Energy Savings for Inert Gas Stripping in Ketone Dewaxing

	Estimated annual savings	
	Utilities	Dollars/Year
A. Stripping steam, pound/hour		
1. Dewaxed oil stripper	3,850	207,000
2. Slack wax stripper	1,180	63,400
3. Ketone fractionator	625	33,600
		304,000
B. Reduced ice load		
1. Refrigeration Kw-hr	60.8	15,300
2. Steam to melt ice, lb/hr	425	22,800
		38,100
C. Reduced solvent rate		
1. Refrigeration, Kw-hr	81	20,400
2. Heat and vaproizing, lb/hr	1,804	97,000
		117,400
D. Increased dewaxed oil, BPOD	50	
Value at $10/barrel		175,000
E. Reduced solvent losses, lb/hr	1.17	4,000
F. Refrigeration savings, Kw-hr	109	27,400
(Higher filtration temperature)		
G. Filter washing, estimated		19,000
H. Reduced maintenance, estimated		97,000
Total savings @ $0.347/bbl		781,900
Energy savings @ $0.278/bbl		486,900
Investment cost, 1983, U.S. $		590,000

Reprinted from Ref. [31] by courtesy of C. W. Nofsinger Co.

VI. OTHER ENERGY REDUCTION TECHNIQUES [20]

A listing of other methods which may be used to reduce energy in lube solvent based processes is shown below:

Use of absorption refrigeration
Integrating process units
Additional evaporation stages
Additional filtration stages
Use of vapor recompression
Use of cogeneration techniques
Membrane separation techniques

Although these methods will reduce energy requirements for base oil manufacture, they appear to be in limited use on the lubricant base oil processing units.

VII. INVESTMENT AND UTILITY REQUIREMENTS

Investment and utility requirements are site-specific and vary widely depending on unit feed capacity, solvent-to-feed ratio, feedstock quality, product quality and the degree of integration of wax manufacture with base oil manufacture. Since the solvent-to-oil ratios are higher for high viscosity stocks than for low viscosity stocks, the investment and utility costs will be higher for manufacture of base oil slates which contain large proportions of the high viscosity base oils. Accurate investment and operating costs can therefore only be determined by a detailed design and definitive estimate for the particular feedstocks, products and product mix to be manufactured. Information concerning investment and utility requirements of the various dewaxing and deoiling processes are available from licensors of the processes with some information being published on a biannual basis in *Hydrocarbon Processing.*

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8

Catalytic Dewaxing Processes

I. INTRODUCTION

The raw paraffin distillates and residual oils leaving the crude stills contain wax and are normally solids at ambient temperature. The deasphalting and refining processes concentrate the wax in the lube feedstocks. Removal of wax from these fractions is necessary to permit manufacture of lubricating oils with the desired low temperature properties. Catalytic dewaxing and solvent dewaxing processes have replaced the older cold settling pressure filtration and centrifuge dewaxing methods in the manufacture of lubricating oils.

The removal of wax from lubricating oil base stocks by solvent dewaxing is expensive from the standpoint of investment and operating costs. Production of low pour point (below about $-25°F$) oils is generally not practical. Several petroleum refiners have patented various catalytic dewaxing (selective hydrocracking) processes for the manufacture of lubricant base oil stocks. The processes which have been commercialized to date were developed by British Petroleum, Chevron and Mobil [1,2,3,4,5,6]. The BP and Mobil processes have also been applied to the dewaxing of both fuels and lube fractions. These processes are more cost-effective and enable manufacturers to obtain lower pour point products than the solvent dewaxing processes. However, the viscosity index is generally lower at the same pour point for catalytically-dewaxed as compared to solvent-dewaxed neutrals prepared from the same feedstock. Dewaxed oil yields are usually lower but in some cases higher than those obtained by solvent dewaxing.

Chevron has recently announced development of a new process, Isodewaxing which is reported to provide higher to equivalent VIs and higher yields than are obtainable from either solvent dewaxing or the first generation catalytic dewaxing processes. This process also permits manufacture of very high VI base oils by isomerizing the wax present in high wax content feedstocks [5,6]. More severe extraction or hydrotreating of distillate feedstocks to the first generation catalytic dewaxing processes is required to produce lube base stock of the same VI as that obtained by solvent dewaxing. The BP process can be used to dewax naphthene feedstocks and low to medium viscosity neutrals and the Mobil Process can be used to process all grades of lube base stocks [1,2]. The Chevron process has to date been used commercially to dewax hydrocracked 100 and 240 neutral oils and is suitable for dewaxing the full range of hydrogen refined feedstocks. The Chevron Isodewaxing Process is reported to be suitable for dewaxing hydrogen refined base stocks and isomerizing slack waxes to produce very high VI base oils [6,7]. Products formulated from the catalytically dewaxed oils are equivalent to those prepared from solvent dewaxed oils and have demonstrated better low temperature properties.

Technical information and details concerning process conditions and design for the catalytic dewaxing processes are currently only available through secrecy agreements with the licensors of the processes.

The characteristics of the first generation catalytic dewaxing processes are as follows:

Investment costs are low compared to solvent dewaxing
Operating costs are low compared to solvent dewaxing
Yield is lower for light neutrals compared to solvent dewaxing
VI is lower for light neutrals compared to solvent dewaxing
Low temperature properties are better compared to solvent dewaxing
Some processes will not dewax all feedstocks
Waxes are cracked to naphtha and LPG
No wax is produced as a by-product
Operating conditions are mild
Hydrogen consumption is low

The characteristics of the second generation catalytic dewaxing processes are summarized as follows:

Investment costs are low compared to solvent dewaxing
Operating costs are low compared to solvent dewaxing
Yield is higher for neutrals compared to solvent dewaxing
VI is higher for neutrals compared to solvent dewaxing
Low temperature properties are better compared to solvent dewaxing
Waxes are cracked to naphtha, middle distillates and LPG
No wax is produced as a by-product

Operating conditions are mild
Hydrogen consumption is low

The process flow and operation of these processes are similar to those of the hydrorefining and hydrogen finishing processes. Hydrofinishing may be required for purification and stabilization of the base oils from these processes.

II. PROCESSES

A. The BP Catalytic Dewaxing Process [1,2,8]

This catalytic dewaxing process uses a proprietary synthetic mordenite containing platinum as the dewaxing catalyst. A simplified flow diagram of the BP process is shown in Figure 8.1 [1]. In this process, the feedstock is mixed with makeup and recycled hydrogen, heat exchanged with effluent streams, heated in a fired heater to the reaction temperature and passed downflow over a fixed bed of catalyst. Hydrogen quench is used to control the reaction temperature by removing heat generated during hydrocracking of the wax and hydrogenation of the hydrocracked products. The reactor effluent is heat exchanged with the

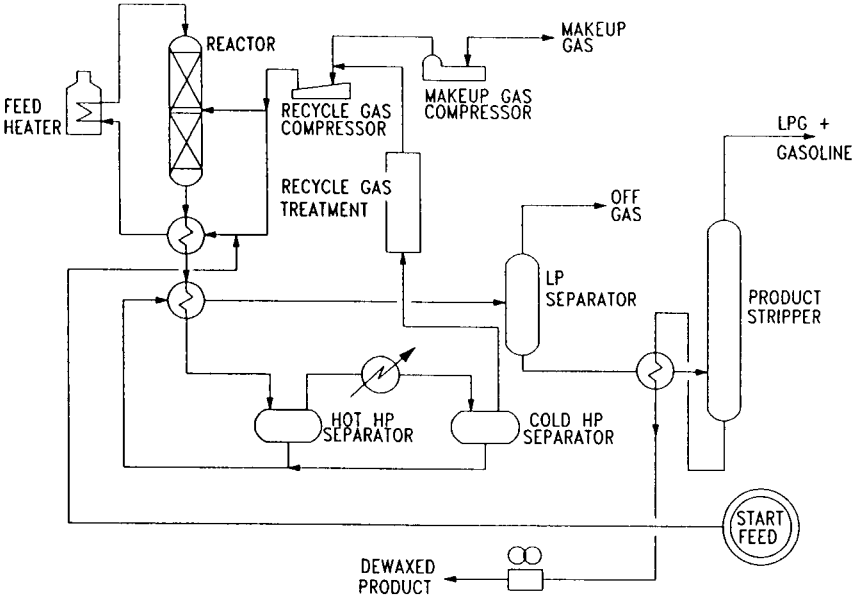

Figure 8.1 Process flow diagram of the BP Catalytic Dewaxing Process. (Reprinted from Refs. [1] and [2] p. 348 by courtesy of British Petroleum and Marcel Dekker, Inc.)

feedstock and separated into a hydrogen rich stream, fuel gas, gasoline and dewaxed oil in a series of separators and stripper. The hydrogen rich gas is purified and recycled in the process. The pour point of the oil is reduced and color of the oil is improved. Nitrogen and sulfur contents are slightly higher than those of the feedstock. Finishing when needed for further color improvement or reduction of nitrogen and sulfur contents may be done using a variety of processes or can be accomplished by addition of a hydrofinishing reactor in series with the dewaxing reactor.

This process can successfully dewax a wide range of naphthenic feedstocks and waxy or partially dewaxed feedstocks from paraffinic crudes to lower pour points than those obtainable by solvent dewaxing. However, it is not a suitable replacement for solvent dewaxing paraffinic feedstocks in the manufacture of high viscosity neutrals, bright stocks or high VI base oils.

1. Process Conditions

The processing conditions used depend on 1) the boiling range, 2) wax content, 3) viscosity and 4) the nitrogen and sulfur contents of the feed. General operating conditions are provided below [1].

Hydrogen partial pressure, psi	300–1500
Liquid hourly space velocity, Vo/Vc	0.5–5.0
Temperature, °F	550–750
Hydrogen rate, SCF/barrel feed	2000–5000

Hydrogen consumption and operating conditions depend on the nature of the feedstock and dewaxed oil pour point.

A commercial unit (a converted hydrotreating unit) of 2000 BPSD was brought on-stream in 1977 and a grassroots unit was brought on-stream in 1983 with additional units in the planning stage at that time [9]. The unit brought on-stream in 1983 was shut down in 1986.

Data from the operation of a 2000 BPSD BP Catalytic Dewaxing Unit have been reported which show that this process is suitable for manufacture of speciality oils, some medium VI lubricating oils and low pour point middle distillates [1,2]. The BP process is not suitable for the dewaxing of high viscosity stocks containing microcrystalline wax [2]. Ramage, et al. [11] have reported data comparing a BP type catalyst with a ZSM-5 catalyst that indicate that this process would not be preferred for manufacture of high VI oils.

2. Investment Costs and Utility Requirements

The investment costs and utility costs for the BP Catalytic Dewaxing Process are summarized in Table 8.1 [1,2].

Table 8.1 Investment Costs and Utility Requirements—British Petroleum Catalytic Dewaxing Process

Unit capacity	10,000BPSD
Capital cost, pounds[a]	3,200,000
Utilities:	
Electricity, kW	680
Heat absorbed, BTU/hour	12,500,000
Medium pressure steam, lb/hr	8,620
Cooling water, lb/hour	165,000

[a] Second quarter, 1981

Reprinted from Ref. [1] by courtesy of British Petroleum.

B. The Chevron Catalytic Dewaxing Process [4,9,10]

The Chevron Catalytic Dewaxing Process was commercialized in 1984 at Chevron's Richmond, California Refinery. The catalyst is most probably a ZSM-5 or a similar zeolite containing a small quantity of a hydrogenation metal. The process flow is similar to a typical two-stage fixed-bed hydrotreater wherein the effluent from the first stage dewaxing reactor is stabilized in a second stage hydrogen finishing (hydrorefining) reactor. Charge stocks to the unit are 100 and 240 neutral hydrocrackates. The VI is 4 to 7 units lower and yield is 4 to 5 weight percent lower for catalytically dewaxed oils as compared to solvent dewaxed oils made from the same feedstock. The process can dewax other hydrocracked feedstocks with no observable deactivation of the catalyst.

The operating conditions and frequency of catalyst reactivation or regeneration for this process are not available and like other processes are no doubt related to the nature of the feedstock. Operating conditions are a hydrogen partial pressure between 2000 and 3000 psi and a liquid hourly space velocity between 0.3 to 3.0 volumes of oil per volume of catalyst for both the dewaxing and hydrogen finishing reactors [9]. Data are not available comparing solvent dewaxing and the Chevron catalytic dewaxing process. However, data from commercial operations were reported by Zakarian et al [4]. This unit was converted to the Chevron Isodewaxing process in the summer of 1993.

C. The Mobil Lube Dewaxing Process [3,11,12,13,14]

The Mobil Lube Dewaxing (MLDW) process is the most widely used catalytic dewaxing process for the dewaxing of lube base stocks. Mobil Distillate Dewaxing (MDDW) is the name of a similar process used for the catalytic dewaxing of fuels fractions [15,16]. The MLDW process can be used to dewax

the full range of feedstocks and was first demonstrated in 1978 using an existing converted hydrotreater in Gravenchon, France. In the spring of 1993, there were ten commercial units in operation including two Mobil units one each in (Australia and the United States) and seven licensed units with additional units in the engineering stage. A simplified flow diagram of the MLDW process is shown in Figure 8.2 [11]. The main differences between the flow of MLDW and BP processes are that a second reactor containing a hydrotreating catalyst is used in the MLDW process to hydrogen finish the dewaxed product effluent from the dewaxing reactor and the use of quench in the BP process.

The proprietary dewaxing catalyst is based on the Mobil developed ZSM-5 zeolite. The second catalyst is a hydrotreating catalyst which is used to saturate the small amount of olefins that are created by the dewaxing catalyst; hydrotreating also improves the color and demulsibility of the finished lube oil. The degree of desulfurization and denitrogenation will depend on the severity of hydrotreating and the catalyst used.

1. Process Conditions

General operating conditions are summarized as follows [3,12,14]:

Hydrogen partial pressure, psi	250–3000
Liquid hourly space velocity, Vo/Vc	0.5–5.0
Temperature, °F	525–700
Hydrogen rate, SCF/barrel feed	500–5000

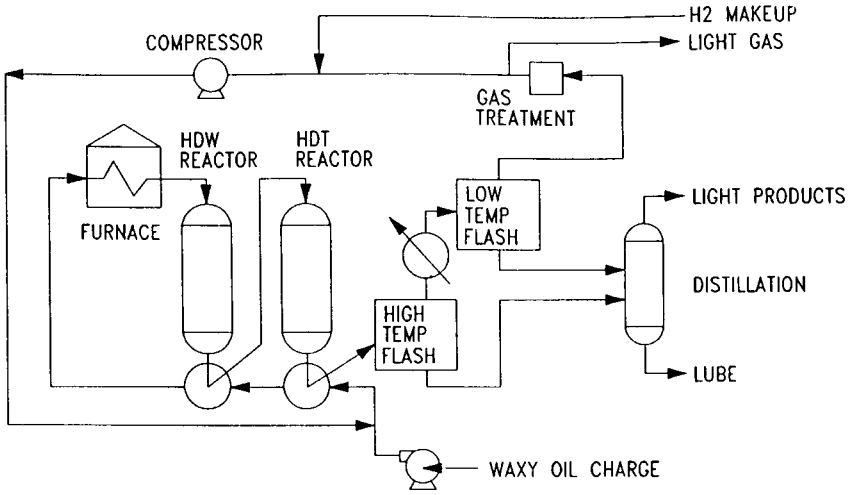

Figure 8.2 Process flow diagram of the Mobil Lube Dewaxing Process. (Reprinted from Ref. [11] by courtesy of Mobil Research and Development Corp.)

Hydrogen consumption and operating conditions are related to the nature of the feedstock and pour point of the dewaxed oil.

Products formulated from MLDW base oils are equivalent to base oils prepared by solvent dewaxing and provide better low temperature properties [17,18,19]. There are currently ten MLDW units in operation with 50,000 BPSD of installed capacity. They range in capacity from 1,500 to 15,000 BPSD in size and represent a variety of process applications and use a variety of feedstocks ranging from bright stock to spindle oils prepared by solvent refining. One of the units is fully integrated with a high pressure lube-hydrocracker [20].

Table 8.2 provides typical product yield data for dewaxing of furfural refined raffinates derived from Arabian Light distillates [20].

Typical dewaxed oil properties and composition for solvent dewaxed and MLDW dewaxed oils are summarized in Table 8.3. These data show that MLDW is more selective as regards removal of normal paraffins and results in a lower VI and yield for the light and heavy neutrals. This also accounts for the comparable VI and higher yield of bright stock.

2. Investment Costs and Utility Requirements [20]

Mobil has recently commissioned an engineering firm to prepare an investment and utility cost comparison for a grassroots base oil plant using MLDW and solvent dewaxing using Arabian Light feedstocks. A summary of the investment costs from this study is shown in Table 8.4. The investment data are battery limits investments for the second quarter of 1992 exclusive of escalation, taxes, spare parts, chemicals startup fees, contingencies, royalty fees and offsite tie-ins. These data show that the base oil plant costs for use of MLDW

Table 8.2 MLDW Yields for Arab Light Distillates

MLDW yields, weight %	Light neutral	Heavy neutral	Bright stock
Hydrogen	−0.19	−0.29	−0.39
C_1+C_2	0.09	0.10	0.12
C_3	2.35	1.61	0.92
C_4	5.06	3.54	2.12
C_5	4.31	3.01	1.78
C_6 − 165C naphtha	10.07	7.00	3.71
165C+ naphtha	2.77	1.74	0.42
Lube	75.54	83.29	91.32
Lube volume %	74.45	82.20	91.20
Lube pour point, °F	0	20	20

Reprinted from Ref. [20] by courtesy of Mobil Research and Development Corp.

Table 8.3 Dewaxed Oil Composition and Properties

	Light neutral		Heavy neutral		Bright stock	
Weight percent	SDW	MLDW	SDW	MLDW	SDW	MLDW
Paraffins	25.2	21.0	18	14	14	13
n-paraffins	0.9	0.2				
Naphthenes	48.3	51.2	39	44	36	40
Aromatics	26.4	27.9	43	42	50	47
Pour point, °F	20	20	20	20	25	25
Typical properties						
Yield, volume %	80	74.5	84	82	86	91
Viscosity index	101	93	95	92	95	95
Pour point, °F	0	0	20	20	20	20

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are about 82 percent of the solvent dewaxing case. The investment costs for use of MLDW is about 50 percent of the combined solvent dewaxing and hydrofinishing base case.

The utility requirements presented in Table 8.5 are also generally lower for MLDW as compared to solvent dewaxing. Mobil has estimated these savings at about $0.50 per barrel [20]. Manpower requirements are also considerably less

Table 8.4 Base Oil Plant Investment Costs

	Solvent dewax	MLDW
Dewaxed oil capacity, BPCD	5480	5480
Light neutral	548	548
Medium neutral	2192	2192
Heavy neutral	1425	1425
Bright stock	1315	1315
Process unit		
Vacuum distillation	Base	+1.5
Propane deasphalting	Base	0
Furfural refining	Base	+2.1
Dewaxing	Base	−21.2
Hydrofinishing	Base	−7.7
Tankage	Base	+1.2
Interconnects	Base	−.09
Total, MM $ U.S. 1992	$143.0	$117.9

Reprinted from Ref. [20] by courtesy of Mobil Research and Development Corp.

Table 8.5 Dewaxing Plant Utilities

	SDW/HFU	MLDW
HP steam lb/hr	126,920	0
LP/MP steam, lb/hr	49,872	7,950
Cooling water, gpm	1,433	2,820
Fuel fired heater, MMBTU	6.65	9.35
Power, kWh	1,292	1,200
Hydrogen, SCFM	238	1,094
Chemicals, bbl/day	20.4	0

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for MLDW as compared to solvent dewaxing and Mobil has estimated that the savings for use of MLDW in place of solvent dewaxing and hydrofinishing at $5.00 to $7.00 per barrel exclusive of process and catalyst royalty charges [20].

D. The Chevron Isodewaxing Process [5,6,7,21]

Chevron has recently announced the development of a new process for the dewaxing of lubricant base oils. It is understood that the process is based on a new proprietary catalyst which isomerizes wax and provides a higher VI than is obtainable by either the solvent dewaxing or other catalytic dewaxing processes.

1. Process Conditions

General operating conditions are summarized as follows [7]:

Hydrogen partial pressure, psi	500–2500
Liquid hourly space velocity, Vo/Vc	0.3–1.5
Temperature, °F	600–700
Hydrogen rate, SCF/barrel feed	Not disclosed
Hydrogen consumption, SCFB	100–500

A comparison of the solvent dewaxed and isodewaxed oil yields and properties is presented in Table 8.6 and 8.7. These data show that the VI of the solvent and isodewaxed oil are essentially equivalent and that the yield of dewaxed oil is greater for isodewaxing. The data also show that the paraffin content of the solvent dewaxed oil is lower. Although VI and yield data are not available for catalytic dewaxing using Chevron's first generation catalyst, it is understood that isodewaxing provides a higher dewaxed oil yield and higher VI than does

Table 8.6 Comparison of Solvent and Isodewaxing of a Hydrocracked Medium Neutral from Alaskan North Slope Crude

Process	Feed	Solvent	Isodewax
Lube yield, volume %		83.1	89.8
Pour point, °F/C	108/42	5/−15	5/−15
Cloud point, °F			15/−10
API gravity		35.8	35.8
Viscosity, cSt @ 100°C		5.79	5.83
Viscosity index		120	121
Compound type, D 2786			
Paraffins, vol %	33.7	29.6	34.4
1-Ring naphthene	34.1	34.5	35.4
2-Ring naphthene	16.3	16.7	18.4
3-Ring naphthene	6.6	6.5	6.7
4+-Ring naphthene	3.1	3.3	3.0
Monoaromatics	0.6	0.6	0.3

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the first generation catalytic dewaxing processes [7]. Data showing that high VI base oils can be made from slack wax are shown in Table 8.8 [7].

Although it has been reported [6] that the Isodewaxing Process can be used to dewax solvent extracted feeds, discussions with Chevron licensing representatives have revealed that very little processing of solvent extracted feeds has been conducted and that the results were inconclusive [7]. A comparison of the product distribution for solvent dewaxing and Isodewaxing is provided in Table 8.9 [7]. A comparison of these data with the data for the MLDW process show that the isodewaxing process produces more naphtha, middle distillate and base oil than does the MLDW process [7].

2. Investment and Utility Requirements

A Chevron publication, *Isodewaxing High-Yield Lube-Oil Dewaxing*, presents the information summarized in Table 8.10.

An estimate of the product distribution, investment and utility requirements for a 17,000 BPSD isodewaxing unit is summarized in Table 8.11 [21].

E. Other Catalytic Dewaxing Processes

Danzinger [22] reported on the commercialization of a new catalytic dewaxing process, Unocal's Unicracking/DW, of atmospheric gas oil and a speciality spindle oil used in speciality oil blending. Danzinger also reports that the technology is readily adaptable to dewaxing other base oil streams. However,

Table 8.7 Comparison of Isodewaxing and Solvent Dewaxing

	Feed	Solvent dewaxing	Isodewaxing
100 Neutral			
API gravity	30.8		34.2
Flash point, COC°F	390		395
Viscosity cSt @ 100°C	4	4.2	4
Viscosity index	96	87	94
Pour point, °C		−12	−12
Cloud point, °C		−11	−9
Sulfur, ppm	<6		
Nitrogen, ppm	1.2		
240 Neutral			
API gravity	28.6		31.8
Flash point, COC°F	470		460
Viscosity cSt @ 100°C	7.2	7.7	6.9
Viscosity index	107	93	102
Pour point, °C		−15	−12
Cloud point, °C		−12	−8
Sulfur, ppm	9		
Nitrogen, ppm	1.5		
500 Neutral			
API gravity	29.6		31.6
Flash point, COC°F	490		518
Viscosity cSt @ 100°C	19	12.1	11
Viscosity index	111	94	106
Pour point, °C		−12	−12
Cloud point, °C		−9	−7
Sulfur, ppm	19		
Nitrogen, ppm	1.2		

Reprinted from Ref. [21] by courtesy of Chevron International Oil Company, Inc.

no data have been published and the process has not as yet been commercially demonstrated.

Ojeda and Ramos [23] have reported laboratory catalytic dewaxing results for a process developed by Instituto Mexicano del Petroleo which has not as yet been commercialized.

III. CATALYTIC DEWAXING FUNDAMENTALS

A. Process Variables

The process variables for the catalytic dewaxing processes are listed in Table 8.12

Table 8.8 Isodewaxing of Slack Wax

	Feed	Isodewaxing
API gravity	35.9	38
Viscosity, cSt @ 100°C		6.28
50°C	6.8	
40°C	13.15	32.8
Viscosity index	172	145
Pour point, °C		−15
Cloud point, °C		−11
ASTM D 2887 volatility		
Volume % 371+ °C		5.5
Yields, wt %		
Fuel gas		4.5
Naphtha		13.6
Diesel		22.5
Lube		60.2

Reprinted from Ref. [21] by courtesy of Chevron International Oil Company, Inc.

Table 8.9 Comparison of Isodewaxing and Solvent Dewaxing Yields

	Isodewaxing plus hydrofinishing	Solvent dewaxing plus hydrofinishing
Chemical H2, SCFB	−375	−175
C1-C3, wt %	0.22	0.2
C4	0.08	0.3
Naphtha	3.4	0
Middle distillate	10.9	0
High VI lube	88	87
Slack wax	0	13

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Table 8.10 Comparison of Dewaxing Processes

	Solvent dewaxing	Catalytic dewaxing	Chevron isodewaxing
Pour point	−10 to −15°C	−10 to −50°C	−10 to −50°C
By-products	Slack wax	Gas + naphtha	Naphtha, jet, and diesel
Capital expense	100 %	60–80 %	65–85 %
Operating expense	100 %	50–60 %	55–65 %

Reprinted from Ref. [21] by courtesy of Chevron International Oil Company, Inc.

Table 8.11 Investment and Utilities Requirements for Isodewaxing and Hydrofinishing

17,000 Barrel per operating day unit	
Product yields per barrel feed	
Chemical H2, SCFB	−375
Fuel gas, EFO barrel	0.005
LPG, barrel	0.01
Naphtha, barrel	0.02
Jet fuel, barrel	0.04
Diesel, barrel	0.08
High VI base oil, barrel	0.88
Feed rate, BPSD	17,000
Capital cost, MM U.S. Dollars	
Makeup compressor	3.2
Reactor loop	35.5
Distillation	11.3
Total on-site	50.0
Total off-site	18.0
Total investment	68.0
Utilities per 1000 barrels feed	
Fuel, EFO barrel	8.59
40 psig steam, M pounds	−7.34
150 psig steam, M pounds	42.3
Cooling water, gallons/minute	34.7
Boiler feed water, gallons/min	1.35
Power, kilowatts	82.4
Shift positions	2
Catalyst life, years	3

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Table 8.12 Catalytic Dewaxing Process Variables

Feedstock composition	Catalyst
Feedstock wax content	Temperature
Feedstock boiling Range	Pressure
Feedstock viscosity	Space velocity
Product pour point	Prior processing

B. Dewaxing Catalysts

The catalysts for catalytic dewaxing are medium pore sized zeolites. The patent literature proposes the use of many different catalysts based on the use of medium pore size zeolites. Examples of commercially available dewaxing catalysts extracted from the *Oil & Gas Journal* [24, 25] are provided in Table 8.13.

The patent literature and discussions with different refiners indicate that the catalysts in use today are based on the use of ferrierite, mordenite, SAPO 11, silicalite and ZSM-5 with ZSM-5 being the most widely used catalyst.

Zeolite catalysts can be used to dewax hydrocarbon fractions by selective hydrocracking of the waxy components. The critical characteristics of lube dewaxing catalysts must be optimized to provide the desired selectivity and catalytic properties that limit the conversion to that of waxy molecules. Restricting the pore size of the zeolite reduces the coking tendency and improves catalyst life. The sizes of several hydrocarbons relative to the constricting pore opening for three zeolites; eronite, ZSM-5 and mordenite are shown in Figure 8.3 [11]. These data show that eronite will permit only normal hydrocarbons to enter the pore openings; ZSM-5 permits some isoparaffins and alkyl sidechains on ring compounds to enter the pore channels; and mordenite permits naphthene and aromatic rings to enter the channels. These data show that eronite permits the entry of normal paraffins but not isoparaffins; ZSM-5 permits both paraffin and waxy isoparaffins to enter the pores and will selectively crack waxy compounds while excluding most lube range components; but mordenite does not exhibit this selectivity and thus cracks more of the good lube compounds [11]. The size of the channel system for ZSM-5 is shown in Figure 8.4 [32] and the channel sizes for some other zeolites are shown in Table 8.14 [26]. It should be noted that Faujasite, a large zeolite, does not have a selective hydrocracking activity for use as a dewaxing catalyst.

Table 8.13 Commercially Available Dewaxing Catalysts

Vendor	Name	Composition
British Petroleum	CDW-12	Platinum on mordenite
Chevron	ICR-401	Proprietary
Chevron	ICR-404	Proprietary
IMP	HDW-10	Platinum-Zeolite
Mobil	MLDW	ZSM-5 and other propietary catalysts
Unocal/UOP	HC-30	Proprietary
Unocal/UOP	HC-80	Proprietary

Prepared from Ref. [14, 24, and 25] by courtesy of the *Oil & Gas Journal* and Mobil Research and Development Corp.

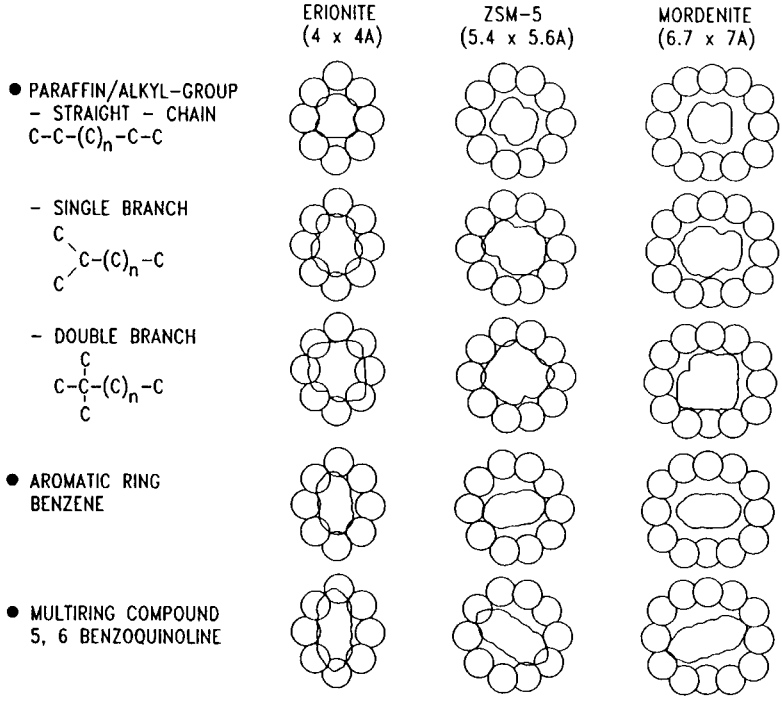

Figure 8.3 Reactant shape selectivity for zeolite catalysts. (Reprinted from Ref. [11] by courtesy of Mobil Research and Development Corp.)

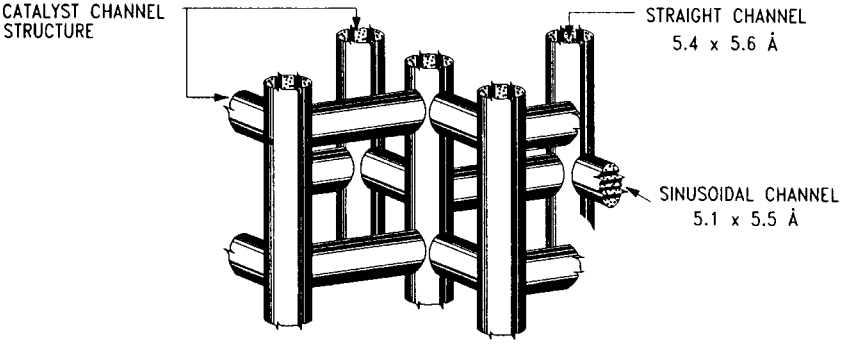

Figure 8.4 ZSM-5 structure. (Reprinted from Ref. [32] by courtesy of Mobil Research and Development Corp.)

Table 8.14 Zeolite Structure Information

Zeolite name	Zeolite type index	Pore opening
Erionite	ERI	3.6 × 5.1
Ferrierite	FER	4.2 × 5.4
		3.5 × 4.8
ZSM-5	MFI	5.3 × 5.6
		5.1 × 5.5
Silicalite	MFI	5.3 × 5.6
		5.1 × 5.5
SAPO 11	AEL	3.9 × 6.3
Beta	BEA	7.6 × 6.4
		5.5 × 5.5
Mordenite	MOR	6.5 × 7.0
		2.6 × 5.7
Faujasite	FAU	7.4 × 7.4

Reprinted from Ref. [26], by courtesy of Butterworth-Heinemann, publishers of *Zeolites*.

Data comparing mordenite and ZSM-5 based catalysts as dewaxing catalysts are shown in Table 8.15 [11]. The data show that the lube yield and VI at the same pour point are lower with mordenite than that obtained with ZSM-5. Catalyst deactivation is strongly affected by coking and poisons contained in the feedstocks which more readily enter and deposit in the pores of mordenite as compared to ZSM-5.

Rollmann and Walsh [27] reported the results of a study using several zeolites which show that the larger the pore diameter, the greater the coking tendency of the zeolite. These data are shown in Figure 8.5 which compares the amount of coke formed with the ratio of the rate constants for cracking of nor-

Table 8.15 Comparison of ZSM-5 and Mordenite Dewaxing

	Feed	ZSM-5		Pt Mordenite	
Lube yield, weight %	0	86	77	73	64
Pour point, °C	+35	−12	−26	−12	−26
Viscosity index	—	94.3	89.4	89.6	77.6
Composition, wt %					
Paraffins	37	—	19	19	14
Naphthenes	32	—	44	45	48
Aromatics	31	36	37	36	38

Reprinted from Ref. [11] by courtesy of Mobil Research and Development Corp.

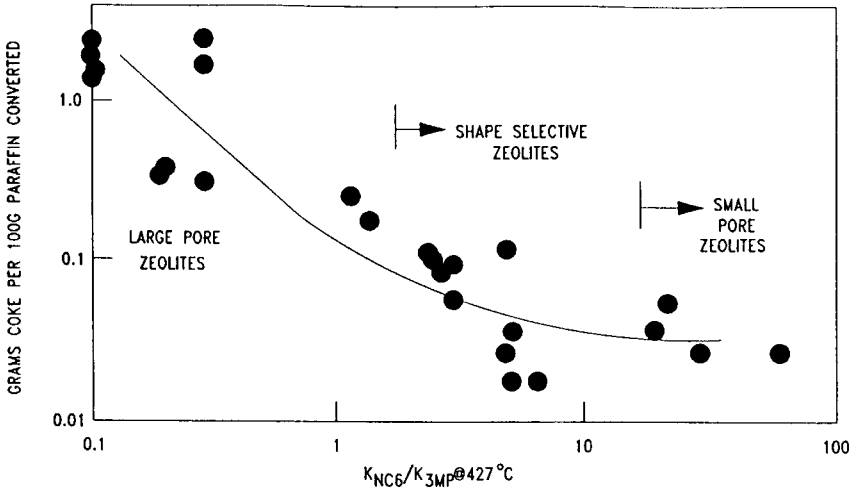

Figure 8.5 Coke yield versus zeolite shape selectivity. (Reprinted from Ref. [27] by courtesy of the *Journal of Catalysis*.)

mal hexane and 3-methyl pentane. It has also been theorized that adding a noble metal to mordenite reduces the coking tendency of mordenite [11]. Studies conducted by Texaco have confirmed that the aging and coking rate of mordenite-based catalysts are lower with noble than with non-noble metals. The aging rate of mordenite with noble and non-noble metals was also improved when nitrogen containing compounds were removed from the feedstock.

C. Process Conditions

The process conditions used depend on the feedstock being dewaxed but are in the range presented in Table 8.16 [1,3,12,14,21]. Technical information and details concerning process conditions and design for the catalytic dewaxing processes are currently only available through secrecy agreements with the licensors of the processes.

D. Feedstock, Wax and Dewaxed Oil Composition

The compositions of waxes contained in lube base stocks are shown in Table 8.17 [28]. These data show that the light SNOs contain waxes which are predominantly normal paraffins and that the heavier oils contain increasing proportions of naphthenes and aromatic waxes. Although the waxes derived from bright stock manufacture are frequently called petrolatums, they are sometimes called malcrystalline waxes because they filter poorly. These waxes have alkyl

Table 8.16 Catalytic Dewaxing Processing Conditions

Variable	British Petroleum	Mobil	Isodewaxing
Pressure, psi	300–1500	250–3000	500–2500
Dewaxing temperature, °F	550–750	525–700	600–750
Hydrofinishing temperature, °F	Not used	475–550	600–700
LHSV, V oil/V cat/hour	0.5–5.0	0.5–5.0	0.3–1.5
Hydrogen rate, SCFB	2000–5000	500–5000	ND
Hydrogen consumed, SCFB	ND	100–200	100–500
Catalyst	Pt Mordenite	ZSM-5	ND
Viscosity grades	Light lubes	All lubes	HT neutrals
Lube yield, volume, %	Feedstock dependent		

ND = Not disclosed HT = Hydrotreated

side-chains which are long enough to give these molecules a high VI and pour points characteristic of normal paraffins.

The relative cracking rates of paraffins by ZSM-5 are presented in Figure 8.6 [12]. The data show that the long chain molecules crack fastest and that the cracking rate decreases as the degree of branching increases.

A comparison of the composition of lube base oils prepared from different grades of feedstocks using solvent dewaxing and MLDW dewaxing as reported by Ramage et al [11] are shown in Tables 8.18 to 8.20. Compositional data for the feedstocks and waxes removed by solvent dewaxing are also presented. The data show that the major wax components of a light neutral are normal paraffins (68%). The MLDW dewaxed oil has a lower normal paraffin content and a higher number of methyl branches than does the solvent dewaxed oil.

Table 8.17 Composition of Waxes from Different Feedstocks

Waxy raffinate for wax composition, vol %	150 SNO	320 SNO	850 SNO	Bright stock
Normal paraffins	59	31	20	0
Iso-paraffins	24	33	29	32
Monocycloparaffins	10	15	17	16
Dicycloparaffins	3	6	9	11
Tricycloparaffins	0	5	7	10
Other paraffins	0	0	9	1
Alkyl benzenes	2	4	9	10
Other aromatics	2	4	0	20

Reprinted from Ref. [28] by courtesy of the *ACS Preprints* and Texaco, Inc.

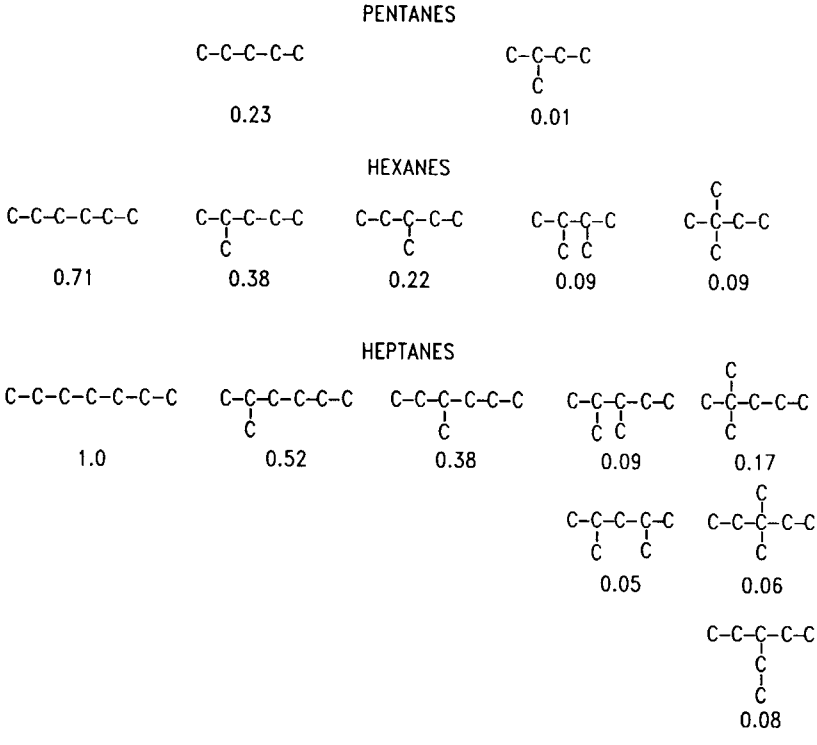

Figure 8.6 Cracking rates for paraffins over MLDW catalyst. (Reprinted from Ref. [12] by courtesy of Mobil Research and Development Corp.)

Table 8.18 Dewaxing of a Light Neutral Raffinate

Composition, weight %	Raffinate	SD wax	SD oil	MLDW oil
Paraffins	37.0	77.6	25.2	21.0
Normal paraffins	15.0	68.0	0.9	0.2
Mononaphthenes	15.3	16.4	14.3	16.5
Polynaphthenes	24.9	2.8	34.0	34.7
Aromatics	23.0	3.2	26.4	27.9
Approximate branches per molecule	3.1	0.1	3.5	4.1
Dewaxed oil				
Viscosity index	—	—	108	98
Pour point, °C	—	—	−6	−6

Reprinted from Ref. [11] by courtesy of Mobil Research and Development Corp.

Table 8.19 Dewaxing of a Heavy Neutral Raffinate

Composition, weight %	Raffinate	SD wax	SD oil	MLDW oil
Paraffins	23	23	18	14
Normal paraffins	2.5	15	—	—
Mononaphthenes	15	37	15	17
Polynaphthenes	24	25	24	27
Aromatics	38	15	43	43
Approximate branches per molecule	3.1	1.1	5.6	5.7
Dewaxed oil				
Viscosity index	—	—	95	89
Pour point, °C	—	—	−6	−6

Reprinted from Ref. [11] by courtesy of Mobil Research and Development Corp.

The VI of the MLDW dewaxed oil is lower because normal paraffins and many slightly branched paraffins are converted to non-lube fractions. The data also show that the paraffinic content decreases and aromatic content increases as the viscosity of the base oils increase from a light neutral through a bright stock. The bright stock is also void of normal paraffins.

The data in Table 8.18 through 8.20 show that paraffin wax content decreases and microcrystalline wax content increases with an increase in molecular weight. The data also show that the VI differences between the MLDW and solvent dewaxed oils decrease as molecular weight or viscosity of the oil increases.

Table 8.20 Dewaxing of a Bright Stock Raffinate

Composition, weight %	Raffinate	SD wax	SD oil	MLDW oil
Paraffins	16	26	14	13
Normal paraffins	<0.2	<2	—	—
Mononaphthenes	14	21	12	14
Polynaphthenes	23	10	24	26
Aromatics	47	43	50	47
Approximate branches Per molecule	5.5	3.1	6.7	6.7
Dewaxed oil				
Viscosity index	—	—	95	95
Pour point, °C	—	—	−3.5	−3.5

Reprinted from Ref. [11] by courtesy of Mobil Research and Development Corp.

E. Effect of Processing Severity

Figures 8.7 and 8.8 compare the change in composition and yield of MLDW dewaxed oils as a function of dewaxed oil pour point [11]. Pour point decreases as process severity is increased. The data show that the major change in composition results from the cracking of paraffins. Since heavy neutrals and bright stock feeds contain very small quantities of paraffins, reduction of the pour point for these feeds results from the cracking of the paraffinic side chains on the naphthenes and aromatics present.

F. Dewaxed Oil Properties

Dewaxed oil properties are dependent on feedstock and yields are dependent on wax content as well as the type of wax contained in the feedstock. Table 8.21 presents some typical data reported by Tung [29]. These data show that MLDW base oil yields are lower for the neutral oils and higher for the bright stock compared to solvent dewaxing. The viscosity of the catalytically dewaxed oils are generally higher and VIs are generally lower than for the solvent dewaxed oils. The VIs of commercially prepared MLDW oils are compared with the VIs of solvent dewaxed oils for the same viscosity grade feedstock [12] as follows:

Viscosity, SUS @ 100°F	100–200	300–500	600–800	2200–2500
Delta Viscosity Index	6–8	4–6	3–5	0

The VIs of MLDW oils are generally lower than those of the solvent dewaxed oils for low viscosity oils and equal to that of the solvent dewaxed high viscosity oils.

Delta dewaxed oil yields, n-paraffin content and viscosity index for solvent dewaxed and MLDW dewaxed oils reported by Smith, et al. [12] and Taylor [28] are summarized in Table 8.22. These data show that the normal paraffin content yield and VI is lower for MLDW as compared to solvent dewaxed oils. The reason for the differences in the delta VI reported by Smith, et al. [12] and Taylor [28] probably relates to the fact that different feedstocks were used, different degrees of fractionation and commercial versus laboratory prepared oils. The higher delta VIs are for the laboratory prepared oils and the lower delta VIs are from commercial operations.

These data show that MLDW works best for heavy stocks; yield and VI are higher relative to low viscosity stocks with little or no VI or yield penalty relative to solvent dewaxing. The lower yield appears to be related to the paraffin content of the feedstocks. This confirms the work of Rowe and Murphy [17]; presented as Figure 8.9, which was developed using different feedstocks.

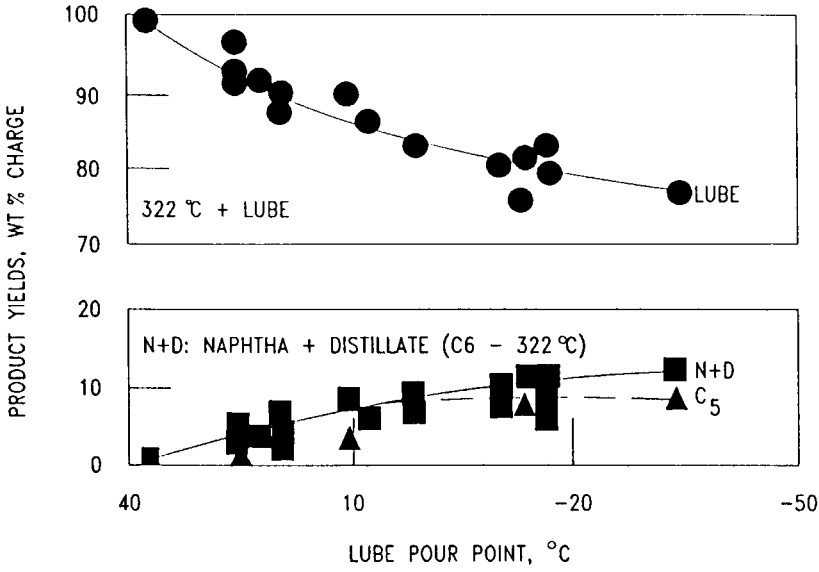

Figure 8.7 Product yield vs pour point for light neutral dewaxing with ZSM-5. (Reprinted from Ref. [11] by courtesy of Mobil Research and Development Corp.)

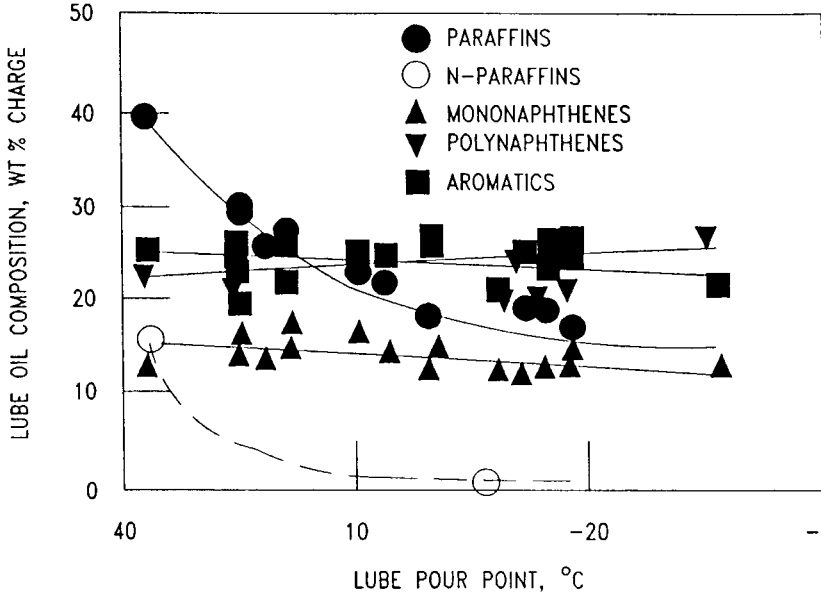

Figure 8.8 Product composition vs pour point for light neutral dewaxing with ZSM-5. (Reprinted from Ref. [11] by courtesy of Mobil Research and Development Corp.)

Table 8.21 Typical MLDW and Solvent Dewaxed Base Oil Properties

	Light neutral		Heavy neutral		Bright stock	
	SDW	MLDW	SDW	MLDW	SDW	MLDW
Yield, volume %	80	75	84	82	86	91
Visc., SUS @ 100°F	160	180	625	691	2896	2867
SUS @ 210°F					162	155
cSt @ 40°C	31	35	119	131	538	533
Viscosity index	107	100	96	90	94	93
Pour point, °F	20	20	20	20	25	25
ASTM Color	0.5	0.5	L2.0	L1.0	5.0	4.0

Reprinted from Ref. [29] by courtesy of Texaco, Inc.

The viscosity and VI of the lube fractions from MLDW dewaxed and solvent dewaxed oils, reported by Smith [30] are shown in Table 8.23 and 8.24, respectively. These data show that ZSM-5 effectively removed the low pour point waxes from the low boiling fractions of the 150 neutral oil but did not remove those waxes from the higher boiling fractions. It is understood that the same phenomenon is exhibited by the isodewaxed oils. Solvent dewaxing removes waxes of like pour point from the light and heavy fractions. The removal of the light boiling n-paraffins by catalytic dewaxing is believed to improve the low temperature properties of the 150 neutral. It is also interesting to note that the VIs of the low viscosity fractions are comparable to those of severely solvent refined naphthene oils and that naphthene oils are sometimes blended with SNOs to improve the low temperature properties of formulated lubricants.

Table 8.22 Comparison of n-Paraffin Content, Yield and Viscosity Index for MLDW and Solvent Dewaxed Oils

Solvent neutral	150	320	850
Delta paraffin content, wt % (SDW-MLDW)	12	6	4
Delta dewaxed oil yield, wt % (SDW-MLDW)	6–8	2–3	0
Delta viscosity index, (SDW-MLDW)[a]	10–13	6–7	4–5
Delta viscosity index, (SDW-MLDW)[b]	6–8	4–6	3–5

[a] Laboratory operations

[b] Commercial operations

Prepared from Refs. [12 and 28] by courtesy of Texaco, Inc. and Mobil Research and Development Corp.

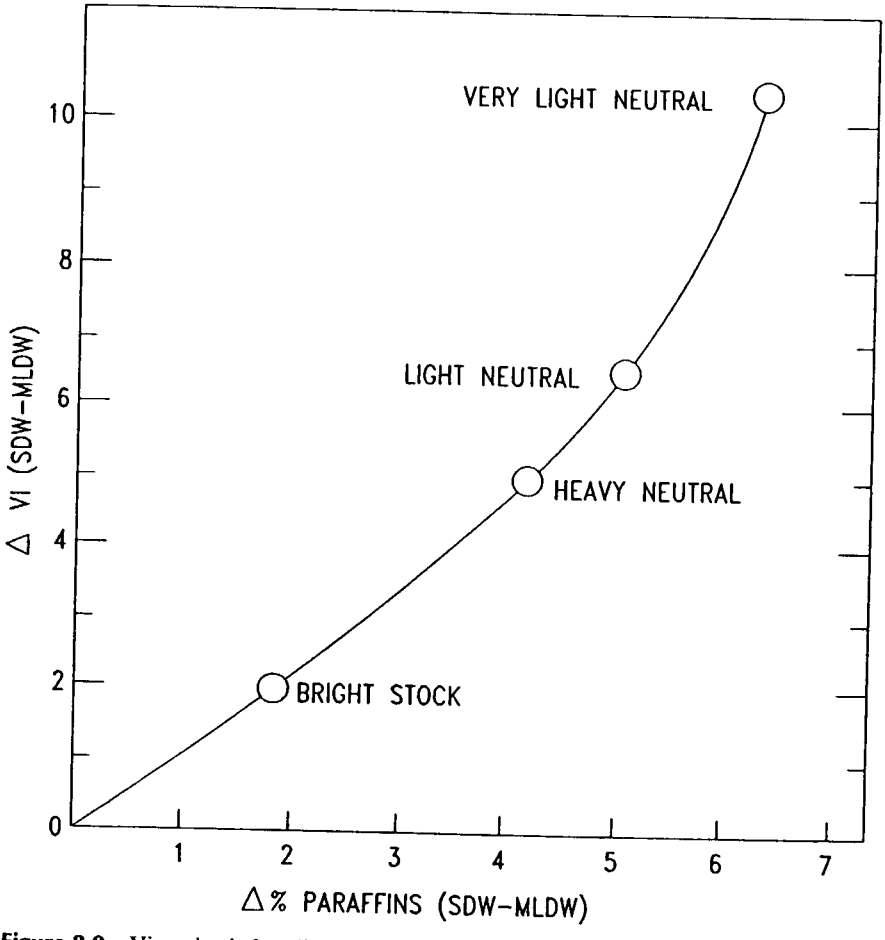

Figure 8.9 Viscosity index difference and paraffin content difference between solvent and catalytically dewaxed oils. (Reprinted from Ref. [17] by courtesy of Mobil Research and Development Corp.)

Table 8.23 Distillation of MLDW Dewaxed Oils

Fraction	One	Two	Three	Four	BTMS	Parent
Yield, volume, %	5	5	5	5	80	100
Pour point, °F	−55	−35	−25	−15	10	5
Visc. cSt @ 40°C	10.58	15.61	18.91	20.95	39.22	32.25
100°C	2.63	3.35	3.79	4.03	5.92	5.26
Viscosity index	72	75	80	81	90	91

Reprinted from Ref. [31] by courtesy of Mobil Research and Development Corp.

Table 8.24 Distillation of Solvent Dewaxed Oils

Fraction	One	Two	Three	Four	BTMS	Parent
Yield, volume, %	5	5	5	5	80	100
Pour point, °F	5	5	5	10	10	10
Visc. cSt @ 40°C	12.33	15.52	16.37	18.92	33.22	28.28
100°C	3.00	3.46	3.63	3.85	5.51	5.00
Viscosity index	72	75	80	81	90	91

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G. Effect of Crude Source

The yield of dewaxed base oil is highly dependent on crude source and directly related to the wax content of the feedstocks and pour point of the dewaxed oil.

H. Catalyst Cycle Time

MLDW catalyst cycle time depends on the quality of the feedstock and feed rate relative to catalyst volume. As the catalyst ages it is necessary to increase temperature to compensate for loss of catalyst activity. The aging rate for both the Chevron and Mobil dewaxing catalysts is too low to measure when dewaxing hydrocracked feedstocks. In addition, the hydrotreating/finishing catalyst aging rate is too low to measure. After the MLDW catalyst reaches the maximum permissible temperature, the feed is removed from the unit and the catalyst is reactivated using a proprietary reactivation procedure. The proprietary reactivation restores catalyst activity to a lower level than that of the fresh catalyst. The commercial aging rate for the dewaxing catalyst (ZSM-5) for repeated cycles is shown in Figure 8.10 [11]. Although these data show a slight loss in activity in the first two cycles and a very gradual loss in activity through as many as 20 cycles with the early versions of the ZSM (MLDW) catalyst, it should be noted that the current (improved) catalyst formulation no longer exhibits a sharp increase in aging rate between the first and second cycle [14]. Commercial experience with the current catalyst which has been in use since mid-1992 shows little to no activity loss between cycles.

Cycle length is related to a number of feedstock properties including nitrogen content. Wax content, final boiling point and the processing method (furfural, phenol, MP or hydrogen refining) also have a strong effect on the time between reactivations [14]. Because of the effects of shape selective catalysts, a direct correlation between nitrogen and aging cannot be developed [14].

Very little of the nitrogen present in the feedstock is actually converted to ammonia. Ammonia is a basic nitrogen compound which will enter the pores of the ZSM catalyst and adsorb on the active sites under MLDW operating

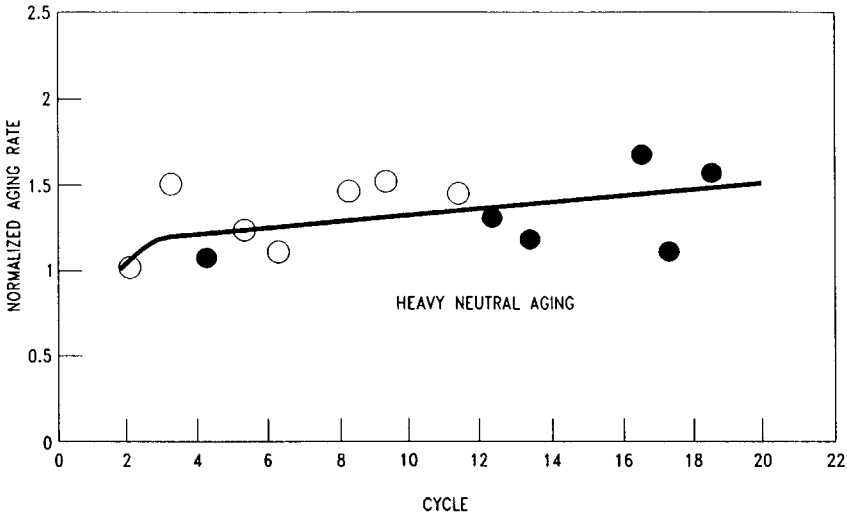

Figure 8.10 ZSM-5 (MLDW) catalyst aging rate. (Reprinted from Ref. [11] by courtesy of Mobil Research and Development Corp.)

conditions. Although this leads to an increase in aging rate, the effect is reversible. When ammonia entering the reactor is reduced, the ammonia will desorb, and the dewaxing temperature will return to normal [14].

With low nitrogen and light to medium viscosity neutrals, a lineout temperature requirement may be achieved. This is a condition where the nitrogen poisons have reached an adsorption/desorption equilibrium on the catalyst surface and are no longer a factor in the aging behavior of the MLDW catalyst [14].

Heavy neutrals and bright stock age at a faster rate than light and medium neutrals. This is a combined impact of the higher final boiling point and higher nitrogen content of the higher viscosity feedstocks. The faster aging rates are largely a result of bulky waxes which have a more difficult time entering the ZSM-5 pores. Wax content is also a major factor in catalyst aging. In general catalyst aging rates increase with increased wax content, increased space velocity and reduced product pour points; all are indicators of reaction severity [14].

Figure 8.11 provides a rough comparison of nitrogen content and cycle time in commercial MLDW operation [14]. These data are for a second cycle operation for cases A–D using the older MLDW catalyst and first cycle operation for Case E using the new generation MLDW catalyst. A number of factors other than nitrogen content are affecting the cycle time and the feeds are processed in blocked operation.

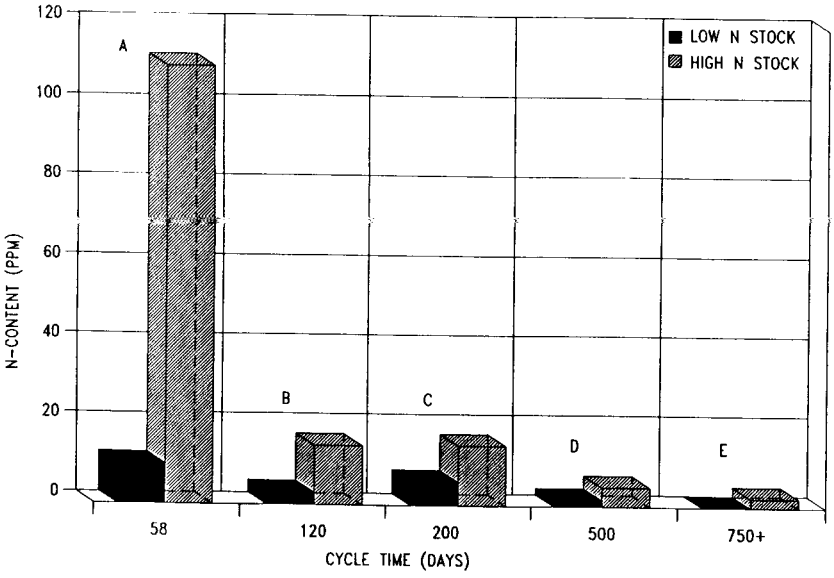

Figure 8.11 Effect of nitrogen on MLDW cycle time. (Reprinted from Ref. [14] by courtesy of Mobil Research and Development Corp.)

Case A achieved a cycle of 58 days while dewaxing solvent refined light neutrals and bright stock which had been previously been solvent dewaxed. This combination of solvent and catalytic dewaxing permitted production of an ultra-low pour point light neutral. Nitrogen contents were in the range of about 10 to 110 ppm.

Case B achieved a cycle of 1230 days while running a previously dewaxed light neutral and some hydrocracker bottoms. This application is not particularly severe. Nitrogen content ranged from low levels to about 15 ppm.

Case C achieved a cycle of 200 days dewaxing a previously dewaxed light neutral (5 ppm nitrogen) and a previously dewaxed bright stock (15 ppm nitrogen). Based on nitrogen content, a shorter cycle would be expected than was obtained with Case B. However, wax content is low making Case C a less severe operation than Case B.

Case D dewaxed hydrocracked light and medium neutral distillates achieved a long cycle of 500 days. This long cycle resulted from both the low nitrogen content of the feedstocks and the fact that heavy neutral and bright stock feeds were not processed.

Case E achieved over 750 days of operation using hydrocracked light to medium neutral distillates with the new generation MLDW catalyst. The new

generation MLDW catalyst has reduced aging rates and extended cycles which have been demonstrated in commercial operation [14].

The effect of incremental reactor temperature on base oil pour point is shown in Figure 8.12 [12]. These data show that for this feedstock, a temperature adjustment of about 1°F results in a change in pour point of about 1°F. Similar relationships, with possible changes in the slope of the line, are obtained with other feedstocks [12].

The stability of the ZSM-5 catalyst to repeated reactivation is further evidenced by the data presented in Figure 8.13 [12]. These data show that the selectivity of the catalyst remains the same following reactivation; the pour point versus base oil yield and pour point versus viscosity index remains the same through 5 reactivations [12]. Subsequent experience has provided the same results through 20 or more reactivations covering a period of over two years without regeneration.

IV. INVESTMENT COSTS AND UTILITIES REQUIREMENTS

The investment costs and utilities requirements are dependent on the crude source, feedstock, degree and type of prior processing, wax content of the feed, product specifications and the process being used. Available data on the British Petroleum, Chevron and Mobil catalytic dewaxing processes are reported in Tables 8.1, 8.4 and 8.5 and 8.11, respectively.

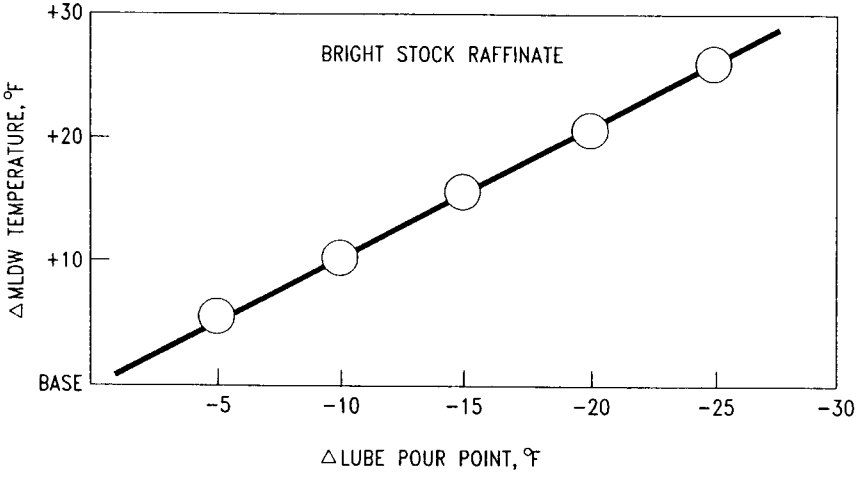

Figure 8.12 MLDW incremental reactor temperature vs base oil pour point. (Reprinted from Ref. [12] by courtesy of Mobil Research and Development Corp.)

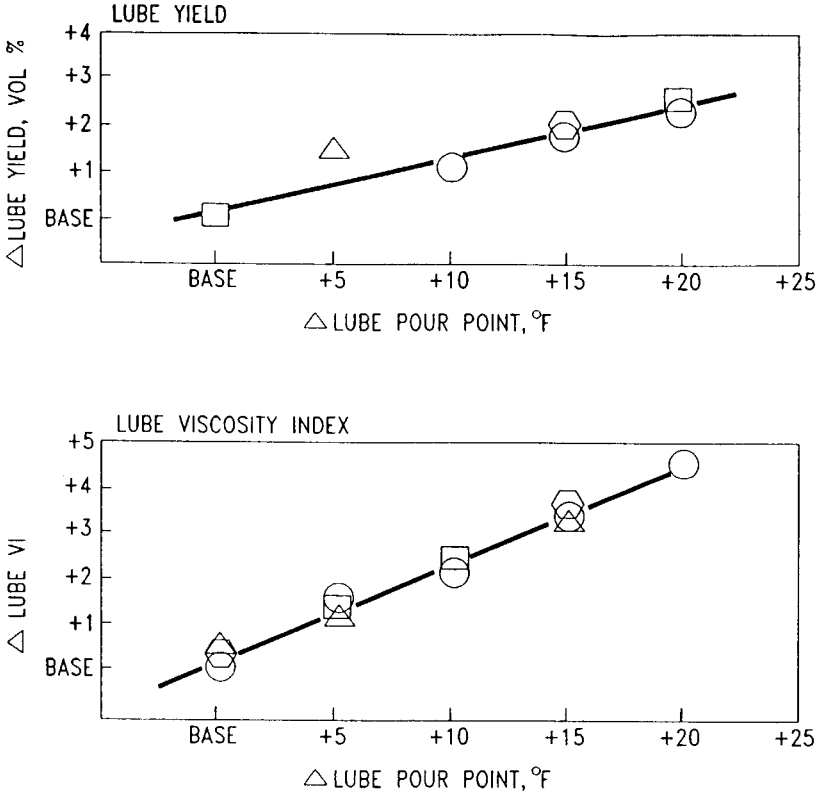

Figure 8.13 Stability of MLDW catalyst with repeated reactivation. ○, Fresh catalyst; ⬡, after one reactivation; □, after two reactivations; △, after five reactivations. (Reprinted from Ref. [12] by courtesy of Mobil Research and Development Corp.)

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9

Lubricant Base Oil Finishing Processes

I. INTRODUCTION

Vacuum distillates and deasphalted oils contain aromatics and other undesirable constituents which result in rapid darkening, oxidation and sludging of the formulated products in service. Chemical, solvent and hydrogen refining processes have been developed and are used to remove these undesirable components and to improve the viscosity index and quality of lube base stocks.

The classical chemical (sulfuric acid and clay refining) processes which were originally used for the refining of lube oil base stocks have been or are being replaced by solvent extraction (solvent refining) and hydrotreating (hydrogen refining) processes because they are 1) more effective for the upgrading of feedstocks, 2) more cost-effective and 3) environmentally more acceptable. Although some refiners still use chemical refining processes, chemical refining is most often used for the reclamation of used lubricating oils or in combination with solvent or hydrogen refining processes for the manufacture of speciality oils such as refrigeration, transformer and white oils. The purpose and effect of the finishing processes are summarized in Table 9.1. The processes used to accomplish these objectives are listed in Table 9.2 and are discussed later.

Table 9.1 Purpose and Effects of Base Oil Finishing Processes

Improve the color	Reduce nitrogen content
Improve color stability	Reduce sulfur content
Improve oxidation stability	Reduce aromatic content
Improve inhibitor response	Improve thermal stability

II. SULFURIC ACID TREATING PROCESSES [1,2,3,4]

Sulfuric acid treating is a chemical treating process in which lubricating oils are contacted with sulfuric acid (85–104 wt%) to (1) improve color and color stability, (2) improve oxidation stability, and (3) remove sulfur, nitrogen and the more active aromatic compounds.

The action of sulfuric acid on lubricating distillates is complex and is generally both chemical and physical in nature. Strong acid attacks almost all of the constituents present in the oil including saturated and aromatic hydrocarbons and sulfur, nitrogen and oxygen compounds. Selective action of the acid on these compounds may be obtained by varying treating conditions, such as reaction temperature, acid concentration, residence time, etc. The chemistry of feedstock components with sulfuric acid is discussed below.

Paraffins are relatively inert; their concentration increases.

Naphthenes are not appreciably attacked; their concentration increases.

Aromatics are more reactive than saturates. Generally, 93 percent acid is the weakest acid suitable for efficient removal of aromatics in lube oil distillates. The use of fuming acid is desirable when complete aromatics removal is required, as in the manufacture of medicinal grade white oils. Treating at higher temperatures (125–150°F, 52–65°C) may be advisable, since sulfonation of aromatics proceeds much faster and the acid is more efficiently used. However, care must be taken to prevent burning and darkening which will occur if the temperature is too high.

Olefins are normally not present in lubricating oil stocks; they are the result of cracking. However olefins are readily attacked by sulfuric acid.

Table 9.2 Base Oil and Wax Finishing Processes

Process	Products
Acid refining	Base oils and waxes
Neutralization	Base oils
Clay treating	Base oils and waxes
Hydrogen finishing	Base oils and waxes
Solvent refining	Base oils

Sulfur Compounds Thiophenes are converted into thiophene-sulfonic acids, which are removed with the acid sludge, at sulfuric acid concentrations of 93 percent and greater. Hydrogen sulfide is oxidized to elemental sulfur by 93 percent (or stronger) sulfuric acid.

Nitrogen Compounds present in lubricating distillates generally consist of amines, amides and minor amounts of amino acids. These compounds are very susceptible to attack by very weak, dilute, sulfuric acid; salts are formed which are easily removed with the acid sludge.

Oxygen Compounds are primarily composed of acids with minor amounts of alcohols and aldehydes. Aldehydes and alcohols are usually oxidized to acids by strong sulfuric acid; the acids are removed during neutralization.

A. Acid-Alkali Refining [1,2,3,4]

Acid-alkali refining also called "wet refining" is a chemical refining process in which lubricating oils are contacted with sulfuric acid followed by neutralization using aqueous or alcoholic alkali. Acid-alkali refining is conducted in a batch or continuous manner. In the older batch processes, depicted in Figure 9.1, the oil to be treated is pumped to a treating agitator and mixed with acid of the desired strength. The oil and acid are mixed by mechanical means or by air blowing and water may be added to assist in coagulation of the acid sludge. The sludge is removed or the oil decanted after settling for a period of several hours. Additional acid is added and the process repeated as needed. The acidic or "sour" oil from this operation is then neutralized using an aqueous or alcoholic neutralizing agent followed by water washing and drying. The main difference in the acid finishing as compared to acid refining is that the quantity

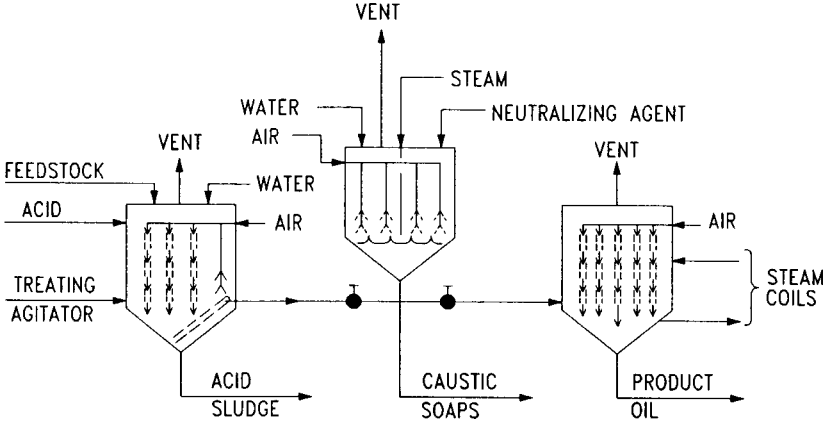

Figure 9.1 Batch acid treating process.

of acid used is usually low (10 or less pounds/barrel) in comparison to the large quantity (25 to 400 pounds per barrel) used in the acid refining processes.

The more modern processes are conducted in totally enclosed treating vessels which eliminate the air pollution associated with the older open treaters.

Continuous acid treating, illustrated in Figure 9.2, involves the same steps as batch refining with the exception that 1) the acid and oil and the "sour" oil and neutralizing agent are mixed with pumps or static mixers, 2) excess acid and sludge and excess neutralizing agent and soaps are removed using centrifuges or centrifugal extractors, 3) water washing is conducted using centrifugal extractors and 4) drying of the oil is conducted in continuous strippers. The advantages for the continuous process over the batch process are 1) higher yields of oil, 2) lower manpower requirements, 3) lower chemical consumption, 4) lower maintenance cost, 5) smaller space requirements and 5) a reduction in air and water pollution.

B. Acid–Clay Refining [1,2,3,4]

Acid–Clay refining also called "dry refining" is carried out in a manner similar to the acid–alkali refining process with the exception that clay is used for neutralization of the "sour" oil. This clay contacting process is used with oils that tend to form emulsions during neutralization and may be conducted in a batch or continuous manner. The bleaching clay is separated from the oil using pressure filters. A simplified process flow diagram for the clay contacting process is provided and discussed in the section on clay treating.

C. Neutralization Processes [3]

Neutralization with aqueous and alcoholic caustic, soda ash, lime and other neutralizing agents is used to remove organic acids from some feedstocks. This

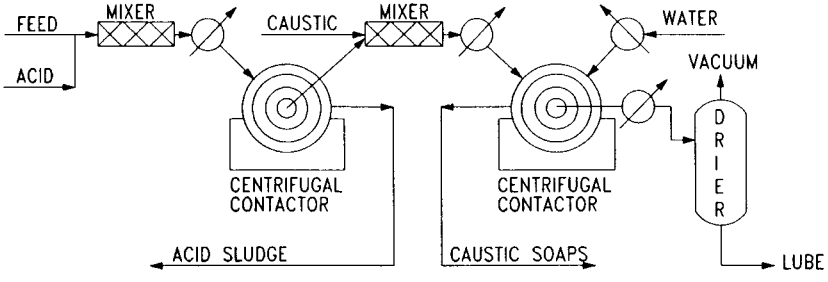

Figure 9.2 Continuous acid treating process.

type of treating can be conducted in a batch or continuous manner as is done in sulfuric acid treating or may be introduced into the crude distillation unit.

III. CLAY TREATING PROCESSES [1,2,3,4,5,6,7]

A. Clay Contacting Processes

Clay contacting is an adsorption process used to remove polar compounds from lubricating oils thus improving color and chemical, thermal and color stability of the lube base oil. The process variables include the type of clay, clay dosage and very high (300–700°F) treating temperature. Clay contacting has been replaced with hydrogen finishing in the manufacture of base oils with the exception that some manufacturers use the process for manufacture of specialty oils.

Clay contacting involves the intimate mixing of oil with fine bleaching clay at elevated temperature for a short period of time followed by separation of the oil and clay. This process may be used alone or in combination with the acid treating process for the finishing and neutralization of lube base stocks. A simplified flow diagram of the process is shown in Figure 9.3.

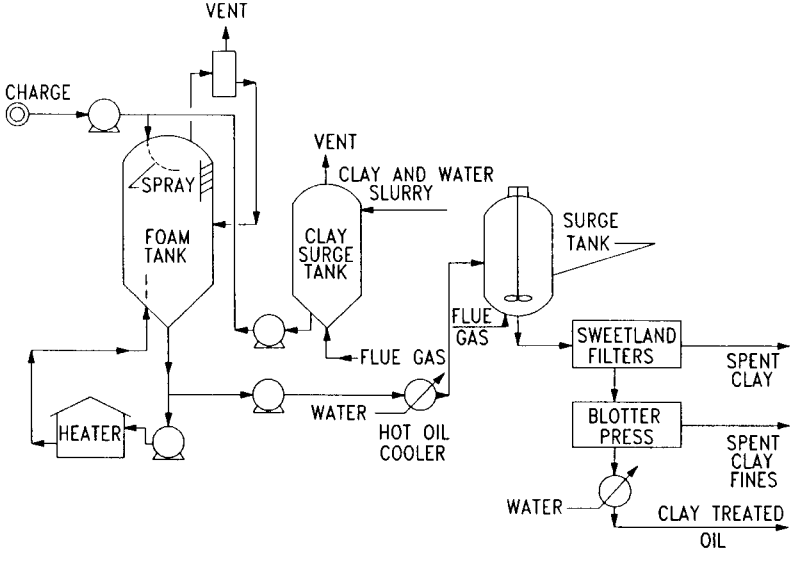

Figure 9.3 Base oil clay contacting process.

B. Clay Percolation Processes [3,5]

Clay percolation is also an adsorption process which may be a continuous process but most commonly a static bed of clay is used to purify, decolorize and finish lube base stocks and waxes. Clay percolation has in large part been replaced by hydrogen finishing but is still in limited use for the manufacture of refrigeration oils, transformer oils, turbine oils, white oils and waxes. Although Attapulgus clay can be used, the most frequently used clay is Porocel, an activated bauxite. The process variables include temperature, flow rate, throughput and type of clay. Clay percolation is a cyclic process consisting of adsorption and regeneration cycles as depicted in Figure 9.4.

The Adsorption Cycle—the initial operation of the adsorption cycle consists of filling the filter vessel with active adsorbent. Once full of adsorbent, feed oil is introduced slowly to force out any air. When the vessel is full of oil, it is usually closed in for about 24 hours to allow the adsorbent bed to readjust itself from any disturbance caused by feed introduction and air removal. The outlet is then opened and the product filtrate is allowed to flow at a controlled rate and throughput, which may range from 0.02–2.0 barrels of oil per ton of clay per hour (BPT/hr) at 25–200 barrels of oil per ton of clay (BPT), respectively. When the filtrate has reached the limiting specification, the flow of feedstock is discontinued and the oil in the bed is allowed to drain. Drainage is followed by washing the bed with solvent to further remove oil. Finally, the adsorbent bed is freed of solvent and some additional oil by steaming. Eight operations make up one adsorption cycle for an individual percolation filter. These operations are summarized in Table 9.3.

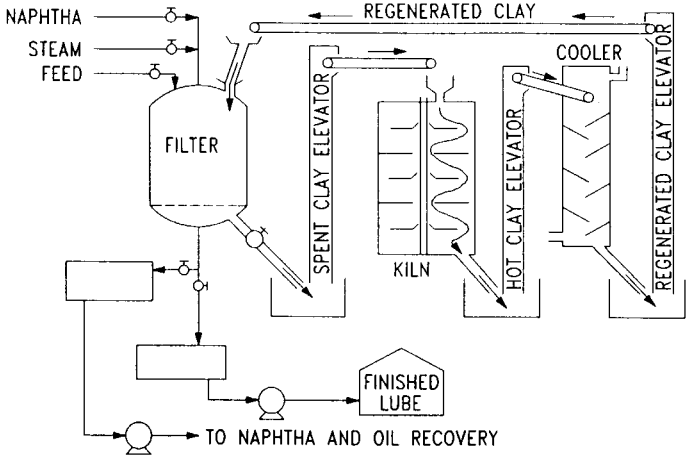

Figure 9.4 Base oil clay percolation process.

Table 9.3 Percolation Adsorption Cycle

1. Charge filter with activated adsorbent.
2. Charge filter with feedstocks.
3. Soak filter (close in for a period of time).
4. Percolate oil to product specification.
5. Drain oil from the filter.
6. Wash the filter with solvent.
7. Steam the filter to remove solvent and oil.
8. Dump steamed clay for regeneration.

The Regeneration Cycle—the regeneration system consists of a kiln and associated clay transporting equipment such as conveyors and elevators. The kiln is used for (1) the initial activation of the new adsorbent entering the system; and (2) regenerating the spent adsorbent for re-use in the adsorption system.

The purpose of the activation operation is to remove free moisture adsorbed during shipping and storage of the adsorbent and to bring the adsorbent to the activity level required for the percolation process. Attapulgus clay is tempered at 500–800°F (260–427°C) with a residence time of 15–30 minutes. Porocel clay is tempered for 15–30 minutes at 700–900°F (371–482°C).

Regeneration is employed to restore the adsorptive efficiency of the adsorbent as nearly as possible to its initial level. The regeneration step includes not only the calcination to remove adsorbed carbonaceous material, but the steps taken prior to calcination to assure that the combustible content of the adsorbent is such that the combustion in the kiln may be controlled. These preparative steps, washing and steaming, are mentioned in the previous section. Even under ideal conditions, the adsorbent loses some of its adsorptive capacity with each repetition of the regenerative calcination. This degradation of efficiency is primarily due to excessive loss of water of hydration which results in modification of crystal structure, pore volume and surface area. Some degradation is due to fusible materials deposited on the adsorbent by the oil being refined. Since the loss of water of hydration and fusion are both functions of time and temperature, it is desirable to limit both as much as possible. Commercial kilns will seldom completely eliminate adsorbed matter below 1000°F (538°C). However, losses of water of hydration increase rapidly above 1100°F (593°C). Therefore, good kiln operation requires temperatures between 1000 and 1100°F (583–593°C) with the lower temperature preferable. Residence times may range between 10 and 30 minutes and should be as short as possible compatible with clean regeneration. Typical properties of these two clays, Attapulgus and Porocel, are presented in Table 9.4 [5].

Table 9.4 Typical Properties of Attapulgus and Porocel Clays

Property	Attapulgus	Porocel
Bulk density, lb/ft^3	34–36	60–63
kg/m^3	54.5–57.7	96.1–101
Water of hydration, wt %	12–15	2–6
Free water, wt %	3–8	2–4
Total volatile matter, wt %	16–20	7–10

Reprinted from Ref. [5] by courtesy of Englehard Corp.

Attapulgus clay is a hydrous magnesium–aluminum silicate and belongs to the "naturally" active class of adsorbents, i.e., adsorptive properties are developed by thermal treatment alone. The degree of activity is determined by the amount of water of hydration retained after thermal treatment. Attapulgus clay may be used to decolorize and neutralize any petroleum oil. It excels in neutralizing traces of strong inorganic acid. Due to the relatively large pores in Attapulgus clay, it is well adapted to the removal of high molecular weight sulfonates, resins and asphaltenes. It is moderately effective in removing odorous compounds and trace metals, but does not strongly adsorb aromatics.

Porocel clay is composed primarily of hydrated aluminum oxide (bauxite) with minor amounts of silica, titania, kaolinite and hematite. Like Attapulgus clay, Porocel belongs to the class of adsorbents activated by heat alone. In addition to decolorization, Porocel reduces organic acidity, affords oils of improved demulsibility, often improves oxidation stability and deodorizes. It is a good refining agent for turbine and transformer oils. A major advantage in using Porocel clay is that while the efficiency declines with successive adsorption–regeneration cycles, it eventually reaches a constant value (typically 60–70 percent of the new clay efficiency). Once this equilibrium efficiency is obtained, no additional reduction in efficiency occurs with further regeneration. Conversely, Attapulgus clay does not attain equilibrium efficiency. The efficiency of Attapulgus clay continues to decline with each successive adsorption–regeneration cycle.

IV. HYDROGEN FINISHING PROCESSES [8,9,10,11,12]

Hydrogen finishing processes are mild hydrogenation processes used in place of the older and more costly acid and clay finishing processes for the purpose of improving color, odor, thermal and oxidative stability and demulsibility of lube base stocks and the purification of waxes. They are fixed-bed catalytic hydrogenation processes used to purify and improve the performance of lubricant base oils and waxes. Unlike the hydrogen refining processes, the hydrogen

finishing processes do not saturate aromatics nor break carbon–carbon bonds at low pressures and temperatures. However, the use of higher pressure will saturate some aromatics and high temperatures will lead to cracking which are not the purpose of the finishing processes; see Chapter 6 for a discussion concerning the hydrogen refining processes.

A. Feedstocks

The feedstocks to hydrogen finishing processes include the following:

Solvent extracted deasphalted oils
Hydrocracked deasphalted oils
Solvent refined distillates
Unrefined distillates
Hydrocracked distillates
Deasphalted oils
Slack waxes
Hard waxes

B. Process Conditions

The operating conditions are dependent on feedstock composition (related to crude source as well as type and severity of prior processing), catalyst and product specifications. A summary of the process conditions is presented in Table 9.5.

The effects of hydrogen finishing temperature and pressure are highly dependent on the quality of the feedstock, product specifications and the type of catalyst used. An increase in temperature or pressure will normally improve neutralization, desulfurization, denitrification, product color and product stability. However, increasing the temperature above some maximum which is related to the catalyst and feedstock quality will degrade the color, color stability, oxidation stability and other properties of the base oil.

Table 9.5 Hydrofinishing Process Conditions

	Processing conditions	
Process variable	Range	Typical
Pressure, Psig	200–1500	500–1000
Temperature, °F	450–650	500–600
Space velocity, Vo/Vc/Hr	0.5–3.0	1.0–1.5
Hydrogen recycle, SCFB	100–5000	300–1000
Hydrogen purity, mole %	50–100	70–80
Hydrogen consumed, SCFB	50–200	70–100
Lube yield, volume %	98+	98+
Catalyst life, years	1–3	1–2

C. Catalysts

A listing of some of the commercially available hydrogen finishing catalysts shown in the *Oil & Gas Journal* [13,14] are presented in Table 9.6. These catalysts consist of the types listed below.

Cobalt–molybdenum on alumina
Nickel–molybdenum on alumina
Iron–cobalt–molybdenum on alumina
Nickel–tungsten on alumina or silica–alumina

Promoters such as fluorides or phosphorus are sometimes used to enhance the activity of these catalysts.

D. Process Flow

A simplified flow diagram of a hydrogen finishing unit is provided in Figure 9.5. The operation of these units is similar to that of the hydrorefining and

Table 9.6 Some Commercial Hydrogen Finishing Catalysts

		Composition		
Manufacturer	Name	Metals	Support	License required
AZKO Chemicals	KF-847	Nickel–molybdenum	Proprietary	No
	KF-8010	Nickel–molybdenum	Alumina	No
	KF-330	Cobalt–molybdenum	Alumina	No
British Petroleum	FF-62	Proprietary	Alumina	Yes
BASF	H 1-80	Nickel	Proprietary	Yes
	M-8-24	Nickel–molybdenum	Alumina	No
	M-8-25	Nickel–molybdenum	Alumina	No
Chevron	ICR-403	Proprietary	Proprietary	May
	GC-26	Proprietary	Alumina	Yes
Criterion	Z-704A	Noble metal	Zeolite	No
	C-614	Platinum	Silica–alumina	No
	C-424	Nickel–molybdenum	Alumina	No
	C-624	Platinum–palladium	Silica–alumina	No
	HDS-3	Nickel–molybdenum	Alumina	No
	HDS-9	Nickel–molybdenum	Alumina	No
	HDS-22	Cobalt–molybdenum	Alumina	No
Englehard	NI-4342	Nickel–tungsten	Alumina	No
	Ni-4352	Nickel–tungsten	Alumina	No
	HPC-60	Cobalt–molybdenum	Alumina	No

Reprinted from Ref. [13] and [14] by courtesy of *Oil & Gas Journal*.

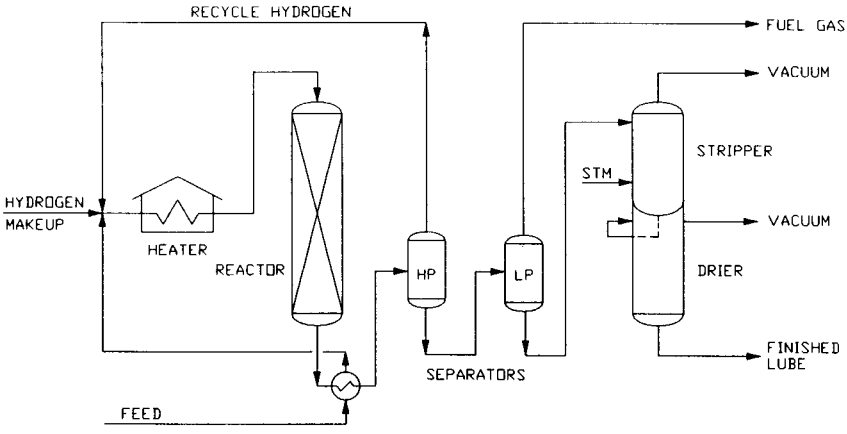

Figure 9.5 Process flow for a hydrogen finishing process.

catalytic dewaxing processes described in the chapters on hydrogen refining and catalytic dewaxing.

E. Effects of Hydrogen Finishing

The effects of hydrogen finishing on the properties of the feedstock are summarized in Table 9.7. The effects of hydrogen finishing temperature on the decolorizing and desulfurization of lube base stocks are shown in Figures 9.6 to 9.9 [15]. It should be noted that although an increase in temperature will usually lead to an improvement in color, excessively high temperatures will darken the oil much like excessive acid contact time or high contact temperature leads to color degradation. Data presented in Figure 9.10 show this effect. Use of excessively high temperature will also lead to cracking of the lube feedstock. Data presented in Figure 9.10 also show that an increase in pressure will improve the color of the base oil.

The work of T. Furukawa reported in the *Bulletin of the Japan Petroleum Institute* [16] presents one of the most complete graphical representations of the

Table 9.7 Effects of Hydrogen Finishing on Product Properties

Decreases sulfur content	Decreases specific gravity
Decreases nitrogen content	Improves thermal stability
May decrease aromatic content	Improves inhibitor response
Increases wax content	Increases pour point
Decreases carbon content	Improves color
Decreases resin content	Improves color stability

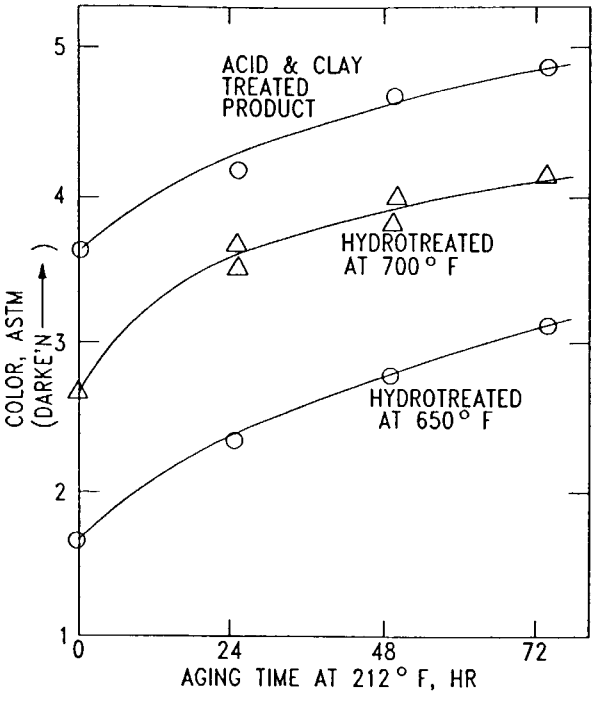

Figure 9.6 Comparison of acid-clay treated and hydrofinished base oil color stability. (Reprinted from Ref. [15] by courtesy of Shell Development Co.)

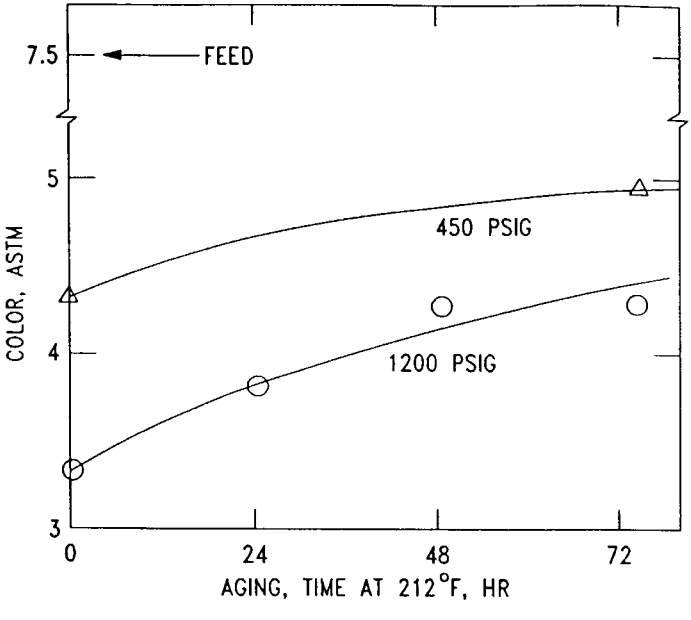

Figure 9.7 Effect of hydrofinishing pressure on color and color stability. (Reprinted from Ref. [15] by courtesy of Shell Development Co.)

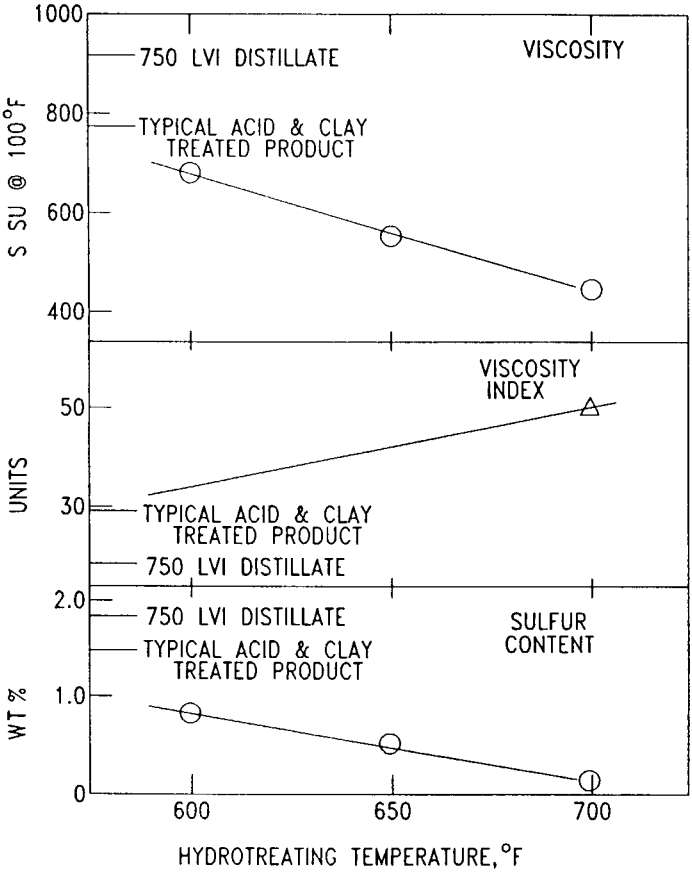

Figure 9.8 Effect of hydrofinishing temperature on viscosity, viscosity index and sulfur content. (Reprinted from Ref. [15] by courtesy of Shell Development Co.)

effect of hydrogen finishing temperature and pressure on several different base oil properties.

It should be noted that the effects of hydrogen finishing are different with different catalysts and that the data reported herein and referenced are only applicable to the catalysts and feedstock and process conditions used. The same general effects will be obtained but the temperatures and pressures at which they occur will differ with different feedstocks and different catalysts.

Figure 9.11 and 9.12 show that the degree of desulfurization and denitrification depends on the catalyst used. The degree of color improvement also depends on the catalyst used and the quality of the feedstock.

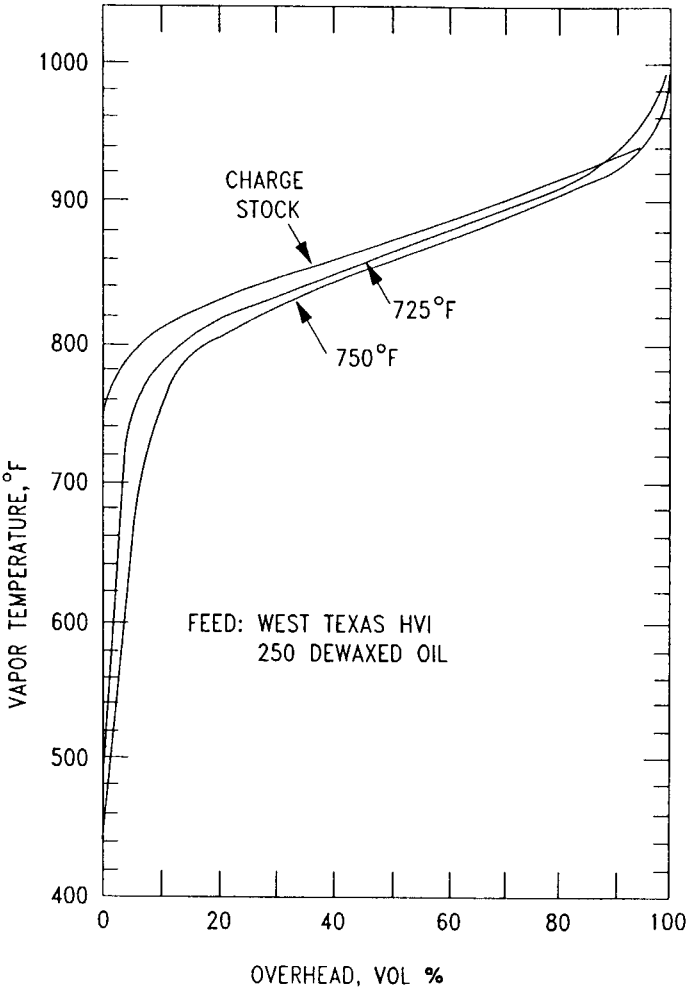

Figure 9.9 Effect of hydrotreating temperature of base oil boiling range. (Reprinted from Ref. [15] by courtesy of Shell Development Co.)

Acknowledged licensors of hydrogen finishing processes include British Petroleum, Chevron, Exxon, IFP and Texaco.

F. Hy-Starting

Hy-Starting, the hydrogen finishing of feedstocks to solvent extraction, is used to improve the yield of refined oil or reduce the sulfur content of aromatic extracts [17,18,19]. When used in this manner the hydrogen consumption is

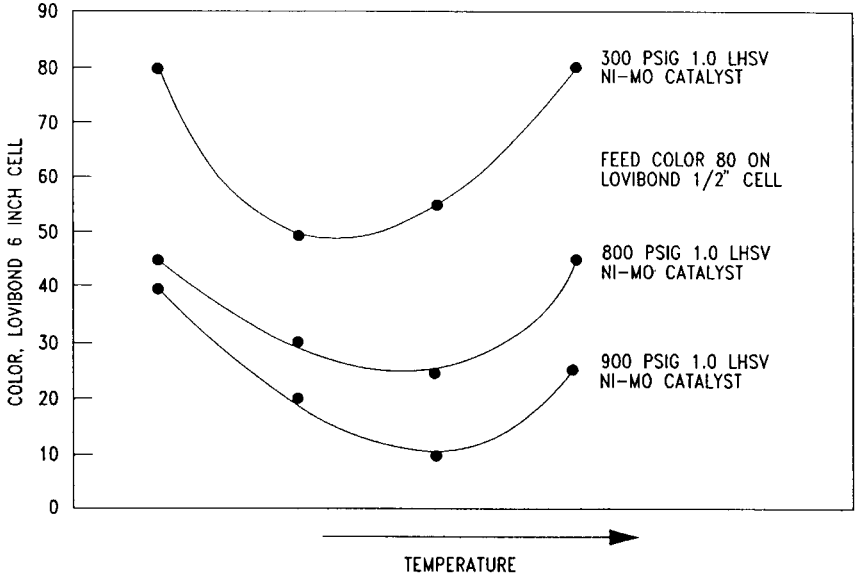

Figure 9.10 Hydrofinishing of a naphthenic distillate.

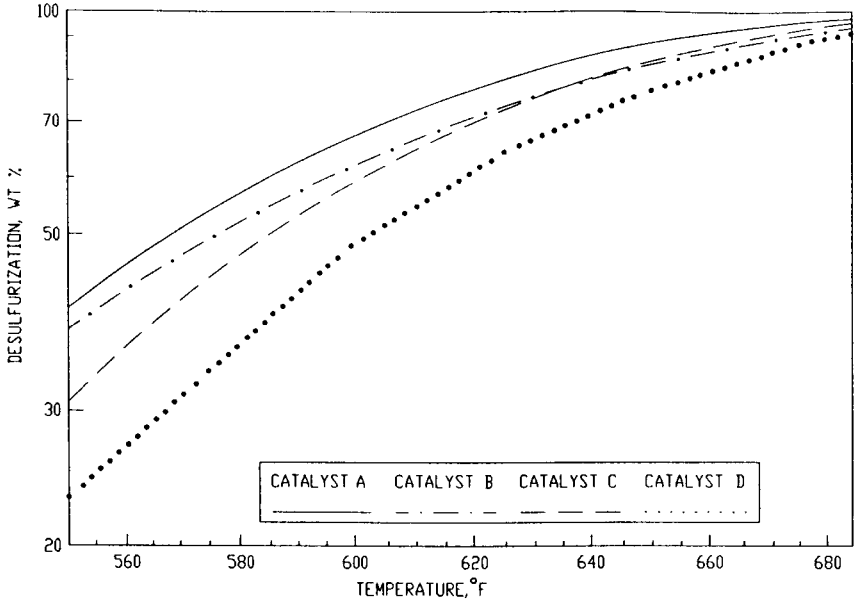

Figure 9.11 Effect of hydrofinishing temperature and catalyst on desulfurization.

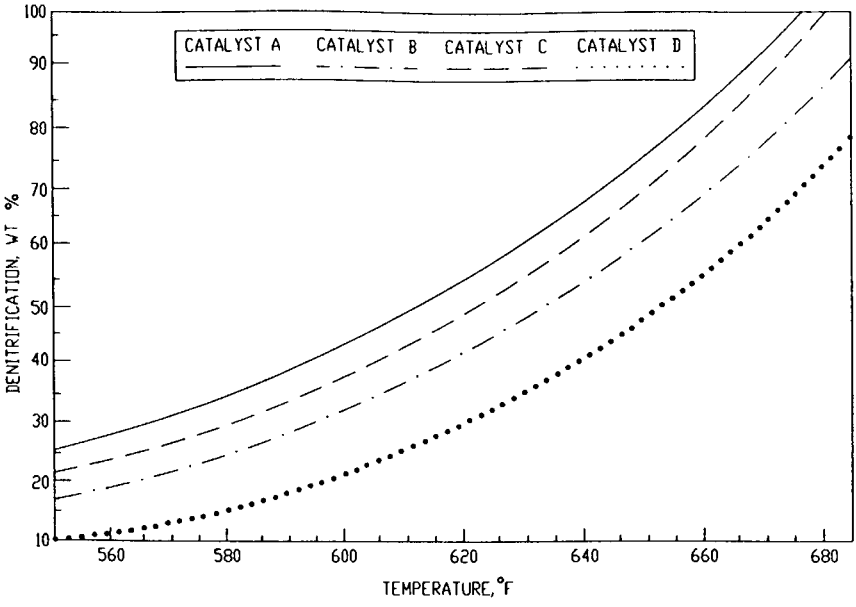

Figure 9.12 Effect of hydrofinishing temperature and catalyst on denitrification.

increased slightly in comparison to hydrogen finishing following solvent dewaxing. However, the size of the extraction unit is reduced and the need for installing finishing units for the manufacture of base oils or desulfurization of extracts (if needed) is eliminated. A comparison of hydrofinishing with Hy-Starting was provided in Table 6.13.

V. WAX FINISHING

Hydrofinishing has replaced clay and bauxite direct contact or percolation processes as the process of choice for the manufacture of wax products which must meet governmental purity specifications; some of these specifications are listed in Table 2.32, Chapter 2.

Wax hydrofinishing offers several advantages over clay treating which include lower operating costs; clay consumption runs from 5 to 100 pounds per ton of product. Spent clay results in a disposal problem and product yield ranges from 75 to 90 percent for the microcrystalline waxes and as high as 97 percent for the light paraffin waxes. Hydrogen finishing yields approach 100 percent [20].

The process conditions and catalysts used for the hydrofinishing of wax are proprietary to the licensors. Suitable catalyst include most of the hydrogen

Table 9.8 Wax Hydrogen Finishing Conditions

Total pressure, psig (bars)	700–1400	(50–1400)
Temperature, °F (°C)	460–660	(250–300)
Space velocity, LHSV	0.5–2.0	0.5–2.0
Hydrogen recycle, SCFB (m^3/m^3)	560–1690	(100–300)
Hydrogen consumption, SCFB (m^3/m^3)	84	(15)

Reprinted from Ref. [21] and [22] by courtesy of Institut Francais du Petrole and BASF.

finishing catalyst listed in Table 9.6 and the hydrorefining catalysts listed in Table 6.18. Operating conditions are in the ranges outlined in Table 9.8 [21,22].

A. Investment Costs

The investment costs for baxuite and hydrogen finishing of waxes as reported by IFP are summarized in Table 9.9 [23]

B. Product Properties

Tables 9.10 and 9.11 present data for the hydrogen finishing of wax using the Exxon Hydrofining process [20]. These data show that the U.S. FDA wax specifications are met using hydrogen finishing. Tables 9.12 and 9.13 present data for hydrogen finishing of waxes using the BASF process [22]. These data also show that the U.S. FDA and the German wax specifications are met by hydrogen finishing. Similar data for hydrogen finishing of waxes have been reported by IFP [21,23] and by Chevron (Gulf) [24].

Table 9.9 Investment Costs for Wax Finishing Processes

	Bauxite treating	Hydrogen finishing
Feed capacity, tons/year	20,0000	20,000
Investment, million francs (1979)	11	7
Yield, weight percent	94	99
Operating costs, francs/ton	Base	−50

Reprinted from Ref. [23] by courtesy of Institut Francais du Petrole.

Table 9.10 Exxon Hydrofining of Paraffin Wax

	Low melt point		High melt point		
	Feed	Product	Feed	Product	Specifications
Wax purity test					
Color	+18 Say.	+35 Say.	20 TR	+35 Say.	+30 Say.
Odor, D 1833	—	1.5	—	1.5	2.0 max
FDA UV. CFR 121.11565		Pass		Pass	Step B
Step A, 280–289 nm	0.366	0.030	0.200	0.035	0.150 max
290–299 nm	0.256	0.025	0.161	0.038	0.120 max
300–359 nm	0.162	0.023	0.106	0.041	0.080 max
360–400 nm	0.011	0.004	0.014	0.008	0.020 max
Other tests					
Melting point, °F	128	128	148	148	—
Oil content, wt %	0.14	0.14	0.15	0.25	0.5 max
API gravity	42.4	42.1	41.0	41.0	—
Viscosity, SUS @ 210°F	38.2	38.2	42.9	42.8	—
Penetration @ 77°F	—	—	13.5	14.0	—

Reprinted from Ref. [20] by courtesy of Exxon Research and Engineering Company.

Table 9.11 Exxon Hydrofining of Microcrystalline Wax

	Feed	Product	Specifications
Wax purity test			
ASTM color D 1500	8.0	1.5	1.5-2.0
Odor, D 1833	—	1.5	2.0 max
FDA UV. CFR 121.11565			
Step A, 280–289 nm	0.462	0.086	—
290–299 nm	0.422	0.091	—
300–359 nm	0.336	0.066	—
360–400 nm	0.049	0.033	—
Step B, 280–289 nm	0.281	0.052	0.150
290–299 nm	0.233	0.054	0.120
300–359 nm	0.171	0.040	0.080
360–400 nm	0.018	0.002	0.020
Other tests			
Melting point, °F	181	182	—
Oil content, wt %	4.6	4.2	5.0
API gravity	33.3	34.0	—
Viscosity, SUS @ 210°F	87.6	86.2	—
Penetration @ 77°F	31.0	33.0	—

Reprinted from Ref. [20] by courtesy of Exxon Research and Engineering Company.

Table 9.12 BASF Hydrofinishing of Macrocrystalline Waxes

Property	Macrowax A		Microwax B	
	Feed	Product	Feed	Product
Specific gravity @ 70°C	0.788	0.776	0.782	0.782
Melting point, °C	57	57	62	62
Visc, cSt @ 100°C	4.1	4.1	5.1	5.1
Oil content, wt %	0.25	0.28	0.40	0.44
Sulfur, ppm	38	<2	360	3
ASTM color	<0.5	—	1.5	—
Saybolt color	—	+30	—	+30
Fluorescence (BGA)	—	pass	—	pass
Hot acid test (BGA)	—	pass	—	pass
PNAs (BGA/CFR)	—	pass	—	pass
UV absorbence (DAB)				
275 nm (max 0.60)	—	0.072	—	0.052
395 nm (max 0.12)	—	0.008	—	0.021
310 nm (max 0.10)	—	0.004	—	0.010

BGA: Mitteilung des Bundesgesundheitsamtes DAB: Deutsches Arzneibuch, 8th edition CFR: U.S. Code of Federal Regulations Reprinted from Ref. [22] by courtesy of BASF.

Table 9.13 BASF Hydrofinishing of Microcrystalline Waxes

Property	Microwax A (a)		Microwax B	
	Feed	Product	Feed	Product
Specific gravity @ 100°C	0.806	0.805	—	—
Specific gravity @ 70°C	—	—	0.815	0.782
Melting point, °C	69	69	55	62
Visc, cSt @ 100°C	16.8	16.9	13.1	5.1
Oil content, wt %	2.5	2.6	5.6	0.44
Sulfur, ppm	550	7	2500	3
ASTM color	6	—	4	—
Saybolt color	—	+19	—	+30
UV absorption (CFR/BGA)				
280–289 nm (max 0.15)	—	0.036	—	0.043
290–299 nm (max 0.12)	—	0.067	—	0.076
300–359 nm (max 0.08)	—	0.064	—	0.066
360–400 nm (max 0.02)	—	0.017	—	0.012

BGA: Mitteilung des Bundesgesundheitsamtes CFR: U.S. Code of Federal Regulations Reprinted from Ref. [22] by courtesy of BASF.

VI. SOLVENT REFINING

Solvent refining is currently being used to stabilize (finish) hydrocracked base oils against the darkening and the formation of haze and sludge on exposure to light. The need and application of this process was discussed in Chapters 5 and 6.

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10

Used Oil Recycling Processes

I. INTRODUCTION

Used oils are lubricating oils or speciality oils which have become unsuitable for their intended use. They may be recycled through the use of reclaiming or re-refining process to obtain useful materials.

Used oil compares favorably with No. 4 and No. 6 fuel oils with the exception that they contain insoluble impurities and high ash contents. Since used oils compare favorably with fuel oils, the major portion of used oils are recycled as fuel after removal of the insoluble impurities. Some used oils are also re-refined and used as base oils for the manufacture of formulated lubricants and products.

The U. S. Environmental Protection Agency (EPA) estimated that 1.3 billion gallons of used oil were produced in the United States in 1988 [1,2]. Table 10.1 presents a summary of the source of used oil in 1988 [2]. Approximately 59 percent entered the used oil management system; 17 percent was dumped or disposed of by industrial and non-industrial sources; 14 percent was disposed of by the do-it-yourselfers and 10 percent was disposed of by the generator.

II. RECLAIMING TECHNIQUES [3,4]

Reclaiming techniques consist primarily of heating, settling, centrifuging, filtering or dehydrating and distillation or a combination of these operations to

Table 10.1 Sources of Used Oil in the United States: 1988

Source	Gallons	Percent
Collected and recycled off-site	770,000,000	59
Non-industrial/industrial unrecycled	219,000,000	17
Do-it-yourselfers, unrecycled	183,000,000	14
Handled by generator	128,000,000	10
Total	1,300,000,000	100

remove solids, water or light hydrocarbons from used oils. Chemical treating with acid, clay, caustic, propane or other chemicals are also used to reduce the metals and sludge contents of used oils for recycle as fuel or for further processing into useful products. Some used oils—mainly industrial oils—are recovered for reuse by heating, dehydrating and filtrating or centrifuging for reuse as lubricants. Frequently this involves the refortification of the reclaimed oil with additives.

III. MAJOR RE-REFINING PROCESSES

Re-refining processes consist of the usual reprocessing methods and base oil manufacturing processes of 1) dehydration and distillation to remove BS&W and light fractions, 2) distillation or chemical treating to remove impurities, 3) hydrogenation or chemical-clay treating and 4) distillation to prepare base stocks.

Alternate methods for the recovery of energy from used oils consist of adding used oils to coker feedstocks or gasification unit feedstocks [2]. It is understood that used oils are currently being used as a portion of the feed to some cokers. Although there is no reference to the running of used oils in admixture with crude oils, it is believed that some small quantities of used oil make their way into some crude oil streams.

Gasification of used oils alone or in combination with other organic material for the manufacture of synthesis gas, a mixture of carbon monoxide and hydrogen, has been proposed [2]. However it is not known if this technique for recovery of energy from used oils has been practiced to any large degree. The major processes used in North America are as follows [5]:

1. Proprietary chemical treatment—distillation—hydrogenation—re-distillation (Mohawk Process)
2. Distillation—hydrogenation—re-distillation (KTI type process)
3. Demetallization—clay treating—distillation—hydrogenation (PROP Process)
4. Distillation—clay treating

The major processes used in Western Europe include [5,6].

1. Distillation—acid—clay
2. Distillation—propane deasphalting—clay
3. Distillation—propane deasphalting—hydrogenation
4. Distillation—demetallization—clay (no published information was found)
5. Distillation—hydrogenation—re-distillation (KTI Process used in Greece)

A summary of the use of lube re-refining processes reported by Fisher [5] is presented below.

Most Commonly Used Re-Refining Processes [5]

Process	No. plants
Acid–clay	350
Ultrafiltration acid–clay	6
Centrifuge acid–clay	3
Phillips PROP	2
Propane deasphalting–IFP	7
Wiped/thin film–hydrogenation	8
Total re-refineries	376

A. The Acid–Clay Processes [3,4,5]

The acid–clay processes have been and continue to be used for the re-refining of used oils. More environmentally acceptable processes have replaced the acid–clay re-refining processes in the USA and will no doubt continue to replace the acid–clay processes on a worldwide basis.

The Acid-Clay processes consist of the steps outlined below.

1. Dewatering and removal of sediment.
2. Treating of the dewatered oil with acid.
3. Removal of the acid sludge.
4. Clay treating of the sour oil.
5. Distillation to prepare different grades of base oils.

B. The IFP Type Processes [3,4,7]

The lube re-refining processes based on the use of deasphalting use the processing steps listed below.

1. Removal of suspended solids, water and light ends.
2. Propane deasphalting to remove the lube fraction from the residue containing asphaltenes, metals and polymerization products.

3. Clay treating or hydrogenation of the lube fraction.
4. Vacuum distillation, if desired, to provide different viscosity grade base oils.

C. The KTI Type Processes [3,8,9]

The Kinetics Technology International (KTI) type processes based on the use of thin film evaporation and hydrogenation are used by several different refiners throughout the world. The processing steps for these processes consist of the following:

1. Removal of suspended solids, water and light ends.
2. Thin film vacuum distillation to produce the lube fraction and a bottoms containing asphaltenes, metals and polymerization products.
3. Hydrogenation of the distillate fraction.
4. Vacuum distillation to provide different viscosity grade base oils.

The vacuum residue from this process is disposed of in asphalt manufacture and may be a major disposal problem/cost if the EPA lists used oil or the residue from this process as a hazardous waste. The major problems with these types of processes involve fouling of the heaters and exchangers and short catalyst life.

D. The Mohawk Process [10]

The Mohawk Process consists of a chemical treatment followed by a KTI type Process. It is in use by Mohawk and by Evergreen; Safety Kleen is reported to be using a similar process [5]. The use of the chemical treatment is reported to extend hydrofinishing catalyst life.

E. The Phillips Re-Refined Oil Process (PROP) [3,11,12]

The Phillips Re-Refined Oil Process, PROP, was licensed and placed in operation by 1) A Texaco affiliate in Mexico, 2) the state of North Carolina, 3) Mohawk and 4) Shell in Canada. The only unit now in operation is the unit located in Mexico.

The PROP process is complex and consists of the following process steps:

1. Mixing of the used oil with an aqueous solution of diammonium phosphate.
2. Heating the mixture to reduce the metals content of the used oil.
3. Metallic phosphates are removed by filtration with diatomateous earth.
4. Light ends are removed by flash distillation.
5. The demetalized oil is heated, mixed with hydrogen and percolated through a bed of clay. Texaco has replaced the clay with nickel-molybdenum catalyst.

6. The percolated oil is then hydrogenated using a nickel–molybdenum catalyst
7. Flashing to remove light ends.
8. Distillation to prepare different grades of base oils.

The major advantage of the PROP process is a high yield (about 90 percent) of the lube range material present in the used oil. This process also generates a neutral phosphate filter cake which can be safely disposed of in a landfill.

IV. OTHER RECLAIMING PROCESSES

Many other processes [3,4] have been proposed but have not been used commercially for the manufacture of lube base oils. The more promising of these processes appear to be the Bartlesville Energy Technology Solvent Extraction (BETC) Process and the UOP Direct Contact Hydrogenation Process.

A. The BETC Process [3,13,14]

This process is similar to the IFP process with the exception that the dehydrated and stripped oil is extracted with a mixture of butyl alcohol, isopropyl alcohol and methyl ethyl ketone instead of propane. Finishing is conducted using either clay treating or hydrogenation.

B. The UOP DCH Process [15]

The UOP DCH Process uses the following processing steps:

1. *Macro-filtration to remove debris.*
2. Mixing and circulating with hot hydrogen.
3. Solids, metals and high molecular weight sludge removal as a liquid phase using a separator.
4. Hydrotreating in a catalytic reactor.
5. Distilling to produce the different viscosity grade base stocks.

C. The Texaco Gasification Process [2]

The Texaco Gasification Process has been proposed for gasification of used oils alone or in combination with other organic material to produce synthesis gas, a mixture of carbon monoxide and hydrogen [2]. This technology is currently in use in over 100 plants and operates at 2500°F assuring that the heaviest organic compound coming from the reactor is methane. There is no stack in the gasifier and no fugitive metals are emitted during the process. In the case of co-gasification the metals contained in the used oil will exit the bottoms in an inert, glass-like slag which is non-leachable and non-hazardous. The economics for the gasification of used oil depends to a large degree on the size of the

plant, location, etc. Teintze [2] reported that when using a existing coal gasifier of about 1100 tons per day making electric power, an investment of $2,000,000 dollars would be required for the addition of tankage, pumps and handling equipment when processing about 1000 BPOD of used oil.

A comparison of the properties of some commercially available re-refined base oils is provided in Table 10.2 It should be noted that these are test results on one receipt of re-refined oil and cannot be considered typical. However it is interesting to note that the VI level of the light neutrals are low; this has been observed when testing other rerefined oils.

Additional data comparing the composition of re-refined oils with virgin base oils were recently reported by Stipanovic, et al. [17]. These data summarized in Table 10.3 show that the re-refined base oils are lower in sulfur and thioaromatic content than the average virgin base oil; some exceptions are evident. Chemical analyses of base oils and testing of fully formulated products indicate that re-refined oils are satisfactory substitutes for virgin base oils in engine oil formulations [17,18]. Considerably more data on re-refined base oils and products formulated therefrom which support this position can be found in many of the references listed at the end of this chapter.

V. ECONOMICS OF USED OIL RECLAIMING

Recently published information on the economics of re-refining lubricating oils has been reported by Magnaboso, et al. [10] and McKeagan [19]. The information presented in Table 10.4 and 10.5 was developed from the work of McKeagan (10). The data in Table 10.4 show that the gross margin for manufacture of re-refined base oils is more attractive than the manufacture of virgin base oils. The main reason for this difference is the cost of the feedstocks.

Table 10.2 Properties of Some Re-Refined Oils

Re-refiner	A		B		C	
solvent neutral	Light	Heavy	Light	Heavy	Light	Heavy
API gravity	32.0	30.0	32.0	30.2	32.1	29.3
Flash, COC°F	385	420	365	455	355	435
Visc. cSt @ 40°C	20.16	55.1	18.3	53.8	16.9	77.4
Viscosity index	85	102	86	85	92	102
Pour point °F	+10	+15	+10	+10	+20	+5
ASTM Color	L0.5	L1.0	L1.0	L1.5	L5.5	8.0+
Aromatics, wt %	16.5	—	19.6	21.7	—	31.9

Reprinted from Ref. [16] by courtesy of ACS and Texaco, Inc.

Table 10.3 Hydrocarbon Type Distribution of Re-Refined Base Oils

Year	Re-refiner	Sulfur	Thio-aromatic	Aromatic	Paraffin	Naphthen
1989	A (Lt SNO)	0.090	0.60	16.7	23.4	59.9
1989	A (Md SNO)	0.080	0.50	14.8	16.7	68.5
1990	B (Lt SNO)	0.100	0.60	16.5	23.4	60.1
1990	B (Md SNO)	0.098	0.60	16.0	23.1	60.9
1990	B (Hv SNO)	0.120	0.70	18.9	19.7	61.4
1990	C (Lt SNO)	0.030	0.80	12.8	17.3	69.9
1990	A (Lt SNO)	0.076	0.80	13.9	22.7	63.5
1990	A (Md SNO)	0.089	0.90	13.9	20.5	65.6
1990	D (Lt SNO)	0.200	1.70	31.9	17.2	50.9
1991	B (Lt SNO)	0.140	1.70	19.5	27.5	53.0
1991	B (Md SNO)	0.110	2.20	21.6	22.6	55.8
1992	B (Lt SNO)	0.059	1.30	18.0	23.3	58.7
1992	B (Md SNO)	0.061	1.30	19.7	17.1	63.2
Average		0.096	1.21	18.0	21.1	60.1
Virgin SNO 100(2)		0.277	1.58	21.9	24.2	54.0

[a] The data reported are the average for 35 samples.
Reprinted from Ref. [17] by courtesy of ACS and Texaco, Inc.

It is also interesting to note that the data reported by McKeagan [19] indicates that neither the solvent refining nor the hydrocracking route is profitable when depreciation costs are included in the total costs.

The data in Table 10.5 show that the re-refining processes are more capital-intensive than conventional lube plants; these differences are no doubt related to differences in the type and size of the units. It should also be noted that the yield of base oil for conventional refining of 37 percent basis distillate would indicate use of a non-lube or less than desirable crude oil; a more reasonable estimate of lube yield would be 50 to 55 percent basis distillate. Use of the

Table 10.4 Gross Margins for Re-Refined and Virgin Base Oils 1990

Processing	Re-refine[a]	SR-SD-HF[b]	HC-SD-HF[a]
Selling price, $/gal	0.90	0.90	0.90
Total costs, $/gal	0.54	0.85	1.04
Gross margin, $/gal	0.36	0.05	−0.14

[a] Plant depreciation costs included.
[b] Plant depreciation costs not included.
Prepared using data from Ref. [19] by permission of Lubrication Engineering.

Table 10.5 Costs for Re-Refining and Conventional Processing 1990

Processing	Re-refine[a]	SR-SD-HF[b,c]	HC-SD-HF[d]
Feed, M gal/year	20,000	207,162	207,162
Yield, volume, %	66	37	37
Base oil, M gal/year	13,200	69,300	69,300
Capital cost, $M	21,500	60,000	160,000
$/gallon	1.63	0.87	2.31
$/barrel	68.41	36.36	96.97
Operating costs, $/gal	0.45	0.14	0.63
Crude costs, $/barrel	—	20.00	20.00
Feed cost, $/gal	0.23	1.67	1.53
Base oil value, $/gal	0.90	0.90	0.90
By-product credit, $/gal	0.14	0.96	1.12

[a] Based on licensors re-refining estimates.
[b] Solvent processing route, U.S. Gulf Coast.
[c] Assumes plant is fully depreciated.
[d] Lube hydrocracking route, U.S. Gulf Coast.
Prepared using data from Ref. [19] by permission of Lubrication Engineering.

higher yields would still indicate that the cost for manufacture of virgin base oils would still be greater than re-refining used oils.

In addition, a comparison of the capital costs for use of solvent refining versus hydrogen refining indicates that the hydrogen refining route is considerably more expensive than the solvent processing route. This difference is greater than the values reported by IFP which are summarized in Table 6.16. A comparison of published economic data for preparing fuels [20] and for gasification [2] of used oil is presented in Table 10.6.

Table 10.6 Comparison of Used Oil Reclaiming and Gasification Processes

Process	Size (gal/year)	Capital (U.S. $)
Gasification	15MM	2 MM
Chemical treatment	10MM	6 MM
Two stage flash distillation	10MM	6 MM
Flash distillation/thin film evaporation	10MM	8 MM
Flash distillation/solvent refining	10MM	7 MM
Blending with virgin fuel oil	10MM	7 MM

Prepared from Refs. [2] and [20] by permission of Texaco, Inc. and the Association of Petroleum Re-refiners.

These data indicate that gasification is the most cost-effective method for recovering energy from used oils. Consideration of the environmental aspects of the processes suggests that gasification is also the more environmentally acceptable process. The reported costs indicate that the investment for blending used oil with fuel oils are overstated or that the investment costs for the other processes are understated when one considers that investments would be lower for blending or gasification when one considers process units would not need to be constructed.

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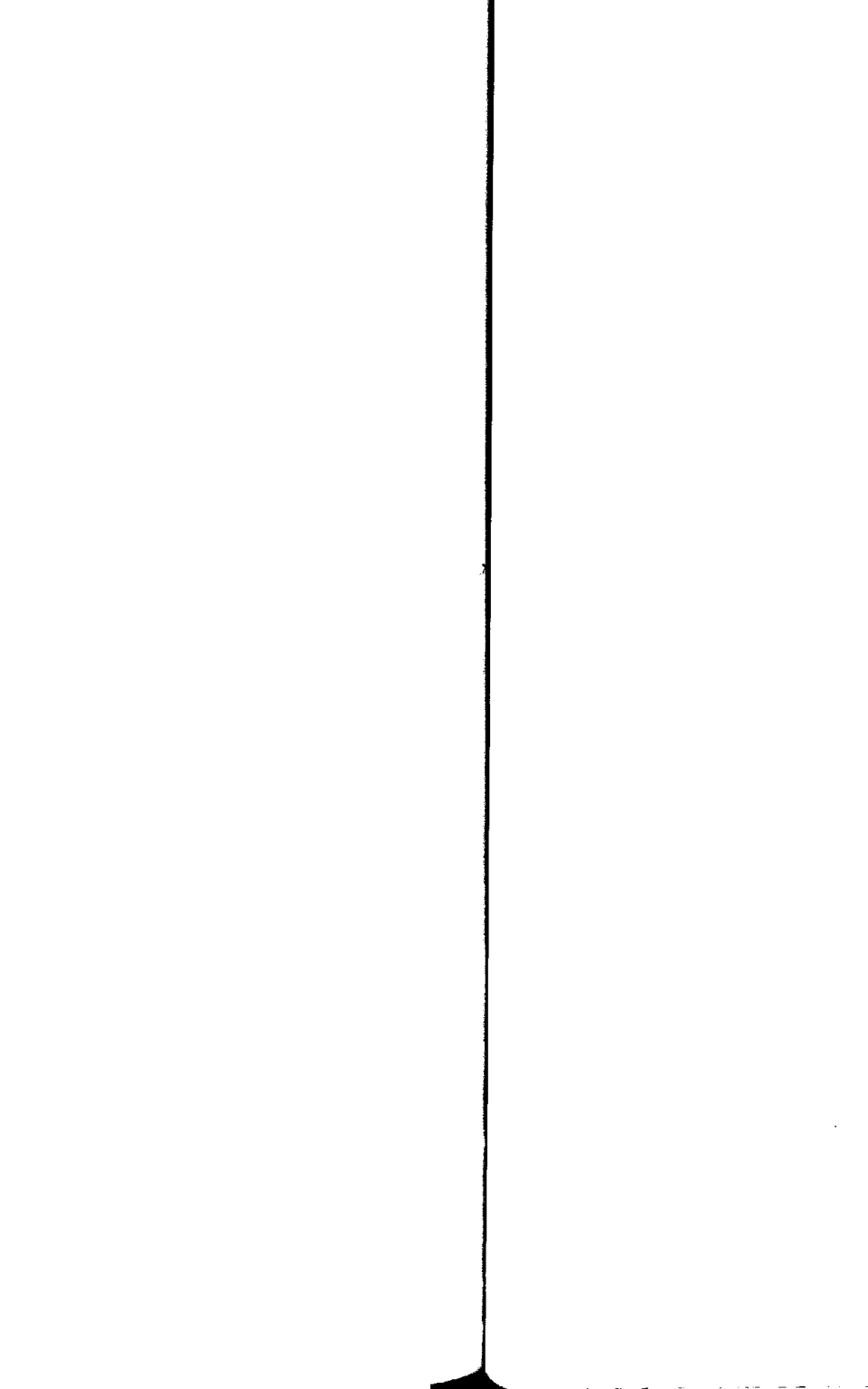

Appendix

I. NOMENCLATURE

ADT	atmospheric distillation tower
ADU	atmospheric distillation unit
ATB	atmosphere tower bottoms; atmospheric residuum
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
ATM	atmospheric
bbl	barrel
BFW	boiler feed water
BPCD	barrels per calendar day
BPOD	barrels per operating day
BPSD	barrels per stream day
BS	bright stock
BS&W	bottoms sediment and water
C	Celsius
CD	catalytic dewaxing, catalytically dewaxed
CDU	crude distillation unit
CFR	Code of Federal Regulations
C.I.S.	Commonwealth of Independent States
CO	cylinder oil
COC	Cleveland open cup
cSt	centistoke

cu ft	cubic foot
cu m	cubic meter
CWTU	chemical waste treating unit
DA	deasphalted
DAO	deasphalted oil
DMSO	dimethylsulfoxide
EDM	electrical discharge machine
EP	extreme pressure
F	Fahrenheit
FDA	Food and Drug Administration
FCCU	fluid catalytic cracking unit
FOEB	fuel oil equivalent barrel
ft	foot
gal	gallon
GC	gas chromatograph
g	grams
HC	hydrocracked
HF	hydrogen finished
HP	high pressure
hp	horse power
HR	hydrorefined
HVI	high VI
Hvy	heavy
J	joule
K	characterization factor
kg	kilograms
kW	kilowatt
kWh	kilowatt hour
lbs	pounds
LHSV	liquid hourly space velocity
LHV	lower heating value
lp	low pressure
LSR	light straight run
Lt	light
M	thousand
m	meter
Max	maximum
MCF	1000 cubic feet
MEA	methyl ethanol amine
Min	minimum
min	minute
mpc	minutes per cycle; filter speed

mpr	minutes per revolution; filter speed
MLDW	Mobil Lube Dewaxing
MM	million
mm	millimeters
mp	medium pressure
MP	N-methyl-2-pyrrolidone
nm	nanometers
NM	normal meters
No.	number
NPO	naphthene pale oil
NPRA	National Petroleum Refiners Association
P	pressure
Pa	Pascal
PAO	polyalphaolefin
ppm	parts per million
psig	pounds per square inch
R	Rankine
RDC	rotating disc contactor
SCFB	standard cubic feet per barrel
SD	solvent dewaxed
SDA	solvent deasphalt
SR	solvent refined
SNO	solvent neutral oil
sq ft	square foot
sq m	square meter
stm	steam
SUS	Saybolt Universal Seconds
Temp	temperature
UHVI	ultra high VI
UV	ultraviolet
Vac	vacuum
VDT	vacuum distillation tower
VDU	vacuum distillation unit
VGO	vacuum gas oil
VHVI	very high VI
VI	viscosity index
Visc	viscosity
Vc	volumes of catalyst
Vo	volumes of oil
vol	volume
VPS	vacuum pipe still
VTB	vacuum tower bottoms

wt	weight
~	about
<	less than
>	greater than
β	beta

II. GLOSSARY OF ACRONYMS AND TERMS

AAMA. The American Automobile Manufactures Association, a trade association of automotive manufacturers with emphasis on qualification and aftermarket testing.

Absorbent. A material having the power, capacity or tendency to absorb.

Absorption. The process by which one substance draws into itself another substance.

ACEA. The Association des Constructeurs Europeens d'Automobiles, a European association of the motor industry.

Acid. A chemical compound which reacts with bases to form salts and water (neutralization). Acids have a sour taste and turn litmus red.

Acidity. The amount of free acid in a substance.

Acid sludge. The residue left after treating petroleum oils or used oil with sulfuric acid for the removal of impurities. It is a black, viscous substance containing spent acid and impurities.

Acid treating. A refining process in which unfinished petroleum or petrochemical products are contacted with sulfuric acid to improve their color, odor, and other properties.

Acid value. A measure of acidity. It is normally expressed as mg KOH/g of sample.

ACS. American Chemical Society.

Additive. A chemical compound added to a lubricant for the purpose of imparting new properties or of enhancing the properties a lubricant already has.

Additive level. The total percentage of all additives in a petroleum product.

Adhesion. The force or forces causing two materials such as a lubricating grease and a metal to stick together.

Adiabatic. A change occurring without loss or gain of heat.

Admix. To add by mixing.

Adsorbent. A material having the power, capacity, or tendency to adsorb.

Adsorption. A process in which a substance concentrates or holds another substance upon its surface by adhesive forces.

ADT. Atmospheric Distillation Tower. The primary distillation tower of a crude distillation unit which operates at or above atmospheric pressure.

ADU. Atmospheric Distillation Unit. Generally, a unit for distilling crude at

or above atmospheric pressure as opposed to operating under a vacuum. (*See also* ADT.)

AGMA. Abbreviation for American Gear Manufacturers Association.

Air entrainment. The incorporation of air in the form of bubbles as a dispersed phase in a bulk liquid.

Alicyclic hydrocarbons. Those which contain a ring of carbon atoms other than the aromatics.

Aliphatic hydrocarbons. Those of open chain structure, as opposed to ring structures.

Alkali. Any substance having marked basic properties. Alkalies are soluble in water, neutralize acids and form salts with them, and turn litmus blue.

Alkylation. The combination of an unsaturated hydrocarbon (olefin) with a saturated hydrocarbon (paraffin or isoparaffin) to form branched chain saturated hydrocarbons. May also apply to the combination of aromatic hydrocarbons with unsaturated hydrocarbons to form branched-chain aromatics.

Almen test. A laboratory procedure used to measure extreme pressure characteristics of fluid lubricants.

Ambient temperature. The existing or surrounding temperature in which a process occurs.

Amine. Pronounced "a-mean." An organic compound containing basic nitrogen. May be toxic and corrosive. The lower molecular weight amines have a smell similar to ammonia.

Amphoteric. Possession of the quality of reacting either as an acid or as a base.

Anhydrous. Free of water, especially water of crystallization.

Aniline point. Temperature at which aniline and oil become completely miscible with each other at equal volumes of aniline and the test sample. This test indicates the paraffinicity of the test sample. ASTM D-611 describes the test procedure for determining aniline point.

Antifoam agent. An additive added to an oil to prevent or reduce foam formation.

Antioxidant. Chemicals added to petroleum products to inhibit oxidation.

API. The American Petroleum Institute, a trade association composed of about 300 firms engaged in all aspects of the U.S. petroleum industry.

API engine service classification. Classifications and designations for lubricating oils for automotive engines developed by API in conjunction with SAE and ASTM.

API gravity. Arbitrary scale for measuring the density of oils which has been adopted by the American Petroleum Institute. °API = (141.5/specific gravity) − 131.5. A high value indicates a light oil.

Apparent viscosity. The ratio of shear stress to rate of shear for a non-Newtonian fluid such as a grease. It is calculated from Pouiseuille's equation and measured in poises. ASTM Method D-1092.

Aromatic. An unsaturated ring compound having a basic 6-carbon-atom ring with either a hydrogen atom or a chain joined to each carbon atom.

ASEAN. The Association of South-East Asian Nations, an economic bloc consisting of Brunei, Indonesia, Malaysia, Philippines, Singapore and Thailand.

Ash content. The percent by weight of residue remaining after combustion of a sample of petroleum using ASTM Method D- 1092.

ASLE. American Society of Lubrication Engineers.

Asphalt. A black to dark brown solid or semisolid material which liquefies on heating. These materials occur in solid or semisolid form in nature and are obtained by refining crude oils. Usually used to describe the residue from vacuum reduction of a vacuum residue, air blowing of a vacuum residue or the residue from deasphalting.

Asphaltic. Essentially composed of or similar to asphalt. Sometimes used as an adjective to describe base oils derived from asphalt containing crude oils.

ASTM. American Society for Testing and Materials, is charged with setting and developing the tests and performance criteria to measure the oil parameters required for new oil categories.

ASTM colorimeter. Apparatus used to determine the color of lubricating oils.

ASTM distillation. Distillations made in accordance with any of the ASTM distillation procedures.

ASTM melting point. The temperature at which wax first shows a minimum rate of temperature change. Also known as the English melting point.

ASTM viscosity. A method of specifying levels for industrial lubricants. Also called the ISO viscosity classification. See ASTM D-2422.

ATC. The Technical Committee of the Petroleum Additive Manufactures in Europe provides a forum for additive companies to discuss developments of a technical and or statutory nature that concern the additive industry.

Atomic weight. The relative weight of an atom of an element referred to carbon-12 taken as a standard with an atomic weight of 12.

Azeotrope. A mixture of two or more liquids which boils at constant temperature and which cannot be separated by ordinary distillation.

Barometer. An instrument for measuring atmospheric pressure. Usually a column of mercury in an inverted sealed tube.

Barrel. A standard unit of measure composed of 42 gallons for the petroleum industry.

Base. Any substance which has the property of neutralizing acids to form salts. It turns red litmus blue.

Batch. Any quantity of material handled or considered as a unit in processing.

Batch treat. A treatment of a limited quantity of material with chemicals to improve quality.

Battery limits. The periphery of the area surrounding any process unit which includes the equipment specific to the particular process.

Bbl. Barrel

Bentonite. The mineral montmorillonite, a magnesium–aluminum silicate used as a treating agent or as a component of drilling mud and in greases.

Benzene or benzol. C6H6, a clear, colorless, flammable liquid aromatic hydrocarbon of many uses in the chemical industry.

Benzene insolubles. The portion of the normal pentane insolubles in used oils which is not soluble in benzene and which may include, in addition to the insoluble contaminants from external sources, the benzene insoluble matter produced by oxidation and thermal decomposition of the oil, additives, and fuel. ASTM Method D-893.

BFOE. Barrels fuel oil equivalent based on net heating value of 6,050,000 BTU per BFOE.

Biodegradable. The microorganism break-down of materials, especially of detergents.

Black oils. Inexpensive products used for lubrication of the roughest kind of bearings.

Blending. One of the final operations, in which two or more components (base oils and/or additives) are blended together to obtain the desired product.

Blocked operation. Operation of a unit, e.g., a VPS, SDU, etc. under periodic change of feedstock; one feedstock is processed at a time rather than a mixture of feedstocks.

Bloom. Florescence: the color of an oil by reflected light when this differs from its color by transmitted light.

Boil up. To rise, bubble or gush up in boiling.

Boil-up rate. The rate at which material is boiled or distilled from a vessel expressed as volume of the condensed liquid per unit of time.

Boiling point. The temperature at which a substance begins to boil or to be converted into vapor by bubbles forming within the liquid.

Boiling range. The range of temperature, usually determined at atmospheric pressure in standard laboratory apparatus, over which the boiling or distillation of an oil begins, proceeds, and finishes.

Bottoms. The liquid which collects in the bottom of a vessel, either during a fractionating process or while in storage.

Boundary lubrication. A state of lubrication existing when conditions for bearings, design, feed, load, and method of application of the lubricant do not permit the formation of a separating lubricant film by hydrodynamic action. Under these conditions adsorption of the lubricant or some surface active component upon the bearing surface or chemical reaction with the surface reduces the metallic contact and determines the character of the frictional resistance.

Box refining. Refining in a small scale mixer–settler counterflow solvent unit in which each section resembles a box.

BPCD. Average flow rates based on 365 days per year.

BPOD. See BPSD.

BPSD. Average flow rates based on actual on-stream time. BPCD/service factor.

Bright. Term generally applied to lubricating oils, meaning clear or free from moisture.

Bright stock. High viscosity, fully refined and dewaxed lubricating oil produced from vacuum residua.

British thermal unit (BTU). The quantity of heat required to raise the temperature of 1 lb. of water 1 degree F.

Bromine index. A measure of the amount of bromine reactive material in a sample; ASTM D-2710.

Bromine number. A test which indicates the degree of unsaturation in the test sample, ASTM D-1159.

BS&W. Bottom settlings and water; the heavy material which collects in the bottom of storage tanks; composed of oil, water, and foreign matter.

BTC. The British Technical Council of the Motor and Petroleum Industries, the U.K. national member of the CEC.

BTU. Abbreviation for British Thermal Unit.

Bulk temperature. A representative temperature of a quantity of material as opposed to a surface temperature.

Bunker "C" fuel. A heavy residual fuel oil used by ships, industry and large scale heating installations. Also called "Navy Heavy" or "No. 6 Fuel".

Burette. A graduated glass tube used for measuring definite amounts of liquids.

Burner oil. A clean burning product obtained from the high-quality kerosene fraction.

Butane. Either of two isomeric, flammable gaseous hydrocarbons, C_4H_{10} of the paraffin series. It is used as fuel, petrochemical feedstock and as a solvent for the deasphalting or vacuum residua and heavy distillates.

Bypass. An auxiliary passage (as a pipe) through which a fluid passes around a particular place or part and returns to the main passage.

CAFE. Corporate Average Fuel Economy.

Calibrate. To determine, rectify or mark the graduations of measuring equipment or instruments.

Calorie. The amount of heat required to raise the temperature of one gram of water one degree C.

Capillary viscosimeter. A viscosimeter in which the oil flows through a capillary tube. An apparatus used to measure the viscosity of an oil.

CARB. California Air Resources Board, the state agency that sets engine emissions in California.

Carbon residue. The amount of nonvolatile carbonaceous residue remaining after destructive distillation under specific test conditions.

Catalyst. A substance which affects, initiates, or accelerates reactions without itself being altered.

Catalytic dewaxing. A catalytic hydrocracking process which uses molecular sieves to selectively hydrocrack the waxes present in hydrocarbon fractions.

CCMC. The Comité des Constructeurs du Marche Commun, an organization of car and truck manufactures within the European Community.

CCS. Refers to Cold Cranking Simulator, ASTM D-5293 method, used to predict whether an oil will permit an engine to crank at low temperatures.

CEC. Coordinating European Council for the Development of Performance Tests for Lubricants and Engine Fuels.

Centistoke. The worldwide unit of kinematic viscosity.

CFR. Coordinating Fuel and Equipment Research Committee composed of engine manufacturing, petroleum refining, petroleum consuming, university, government and other technical persons who supervise cooperative testing and study of fuels for the Coordinating Research Council, Inc. (CRC).

Characterization factor. An index of feed quality used for correlating data based on physical properties. The Watson (UOP) characterization factor is defined as the cube root of the mean average boiling point in degrees Rankine divided by the specific gravity.

Clay treating. A clay adsorption process operated at elevated temperature and pressure used to neutralize or improve the color and stability of a lube base oil.

Cloud point. The temperature at which paraffin wax or other solid substance begins to crystallize out or separate from solution, imparting a cloudy appearance to the oil when the oil is chilled under prescribed conditions.

CMA. Chemical Manufacturers Association; the Additives Panel for this trade association developed a Product Approval Code of Practice to help ensure that a particular engine lubricant meets specified performance specifications through the use of engine tests and procedures.

Coastal oils or crudes. Naphthenic-type petroleum oils obtained from regions near the coast of the Gulf of Mexico.

Complex soap. A soap wherein the soap crystal or fiber is formed usually by co-crystallization of two or more compounds.

Compounded oil. Mineral oils containing additives or fatty materials.

Compounding. The mixing of stock oils and additives to impart special properties. See Blending, Formulation.

Conradson carbon. A test used to determine the amount of carbon residue left after the evaporation and pyrolysis of the test sample at specified conditions. ASTM D-189.

Consistency hardness. The degree to which a plastic material such as lubricating grease resists deformation under the application of force.

Corrosion. The gradual eating away of metallic surfaces as the result of oxi-

dation or other chemical action. It is caused by acids or other corrosive agents.

Cracking. A phenomenon by which large oil molecules are decomposed into smaller, lower-boiling molecules; at the same time certain of these molecules, which are reactive, combine with one another to give even larger molecules than in the original stock. The more stable molecules leave the system as cracked gasoline, but the reactive ones polymerize, forming tar and coke.

CRC. Coordinating Research Council Inc., an organization supported jointly by the API and the SAE which administers the work of the CFR and other committees pertaining to correlation of test work on fuels, lubricants, engines, etc.

CUNA. The Commissione Technica di Unificazione nel l'Autoveicolo, the Italian national organization member of the CEC.

Cut. The portion or fraction of a crude oil boiling within certain temperature limits.

Cut point. The temperature limit of a cut or fraction, usually but not limited to a true boiling point basis.

Cylinder stock. The residuum remaining in a still after the lighter parts of a crude have been vaporized; originally used for lubricating the cylinders of steam engines.

DAP. The Detroit Advisory Panel of the API which liaisons between the OEMs and the various fuels and lubricants committees of the API.

Deasphalted oil. The extract or residual oil from which ashphalt and resins have been removed by an extractive precipitation process called deasphalting.

Deasphalting. A process for removing asphalt from reduced crude or vacuum residua (residual oil) which utilizes the different solubilities of asphaltic and nonasphaltic constituents in light hydrocarbon liquids, e.g., liquid propane.

Density. The mass of a unit volume of a substance.

DEO. Diesel engine oil.

Deoiling. Reduction in quantity of liquid oil entrained in solid wax. The oil may be removed by draining or by a selective solvent.

Detergent oil. A lubricating oil possessing sludge dispersing properties for use in internal combustion engines. This property is imparted to an oil by certain additives which cause the oil to hold particles in suspension and promote engine cleanliness.

Dewaxing. The removal of wax from oil. Solvent dewaxing in which a number of different solvents can be used has the following steps: feedstock is mixed with solvent and chilled; wax precipitated from solution is separated; solvent is recovered from wax and dewaxed oil. Wax separation is accomplished by filtration, centrifuging or settling.

Dielectric strength. A measure of the adequacy of insulating materials to resist electrical stresses. Testing of petroleum products is done with an apparatus as described in ASTM Method D-877.

DIN. Deutsches Institut fur Normung, One of the German technical subcommittes which develops and publishes standard test methods.

Dispersant. A dispersing agent, an additive compatible with the base fluid which holds a very finely divided third substance in a dispersed state.

Distillate. Product of distillation collected by passing vapors through a condenser.

Distillation. The process of heating a liquid to its boiling point and condensing and collecting the vapors.

DKA. Deutscher Koordinierungsausschussim Coordinating European Council, the German member of the CEC.

Dropping point. The temperature at which a drop of material falls from the orifice of the test apparatus under the conditions of ASTM D-566 (IP 132) and ASTM D-2265.

EC & EC-II. Energy conserving and energy conserving II ratings for crankcase oils.

EFT. The Engine Fuels Technical Committee of the CEC which supervices activities of the CEC working groups dealing with engine fuels.

ELTC. The Engine Lubricants Technical Committee which supervises the activities of the CEC working groups dealing with engine lubricants.

EMA. The Engine Manufacturers Association for engine manufactures for all applications except passenger cars and airplanes.

Endothermic reaction. A reaction in which heat must be added to maintain the products and reactants at a constant temperature.

End point (EP). Upper temperature limit of a distillation.

EOLCS. The API Engine Oil Licensing and Certification System.

EPA. The U.S. Environmental Protection Agency.

EP agent. An additive introduced into a lubricant to impart load carrying or anti-wear properties.

EP lubricants. Lubricants to which additives have been included to impart the ability to withstand extreme pressures.

Exothermic reaction. A reaction in which heat is liberated. Acid treating and hydrogenation processes are exothermic.

Extract. In solvent refining processes, that portion of the oil which is dissolved in and removed by the selective solvent; the solvent rich phase.

Extraction. The process of separating a material, by means of a solvent, into a fraction soluble in the solvent and an insoluble residue.

Extreme pressure (EP) property. The ability of a lubricant to reduce scuffing, scoring and seizure of contacting bearing surfaces when applied loads are high.

FBD. Final boiling point. See End point.

Feedstock. Crude oil or a fraction thereof to be charged to any process equipment.

FFV. Flexible-Fuel Vehicle or Fuel-Flexible Vehicle refers to vehicles designed to run on fuels ranging from 100 percent gasoline to M85 (85 percent gasoline/15 percent methanol. Sometimes called VFW or Variable-Fuel Vehicle.

Fiber. The form in which soap thickeners occur. Some soaps crystallize in threads which are of the order of 20 or more times as long as they are thick.

Filtrate. The liquid which has passed through a filter, i.e., the product from a filtration process.

Fire point. The lowest temperature at which a petroleum product forms vapors, under specified experimental conditions, at a rate sufficient to maintain continuous burning when ignited with a small flame. Two methods are used; the Cleveland Open Cup (COC) method ASTM D-92 and the Pensky-Martens (PM) or closed cup method ASTM D 93.

Flash point. The lowest temperature at which a petroleum product forms sufficient vapors, under specified experimental conditions, to cause a flash or slight explosion when ignited by a flame.

Floc point. The temperature at which wax or solids separate as a definite floc.

Flux. The addition of a small amount of material to a product to meet some product specification.

FOE. Fuel oil equivalent; the heating value of a standard barrel of fuel oil equal to 6.05×10^6 Btu; LHV.

FOEB. See FOE.

Foots oil. Oil and low melting point wax removed from a slack wax in the manufacture of a hard wax.

Fractionation. Separation by successive operations, each removing from a mixture some proportion of one of the substances. The operation may be precipitation, crystallization, distillation, etc.

FRU. Furfural Refining Unit. Generally refers to a solvent extraction unit which uses furfural as the solvent.

Furfural. An aldehyde obtained from corn shucks, wheat, or oat hulls, used in an extraction process for removing aromatic, naphthenic, olefinic and unstable hydrocarbons from a lubricating oil charge.

Furfural refining. A widely used solvent refining process using furfural. This process was developed by Texaco.

FZG test. A German gear test for evaluating EP properties.

GHV. Gross heating value. The heat produced by complete oxidation of a material at 60°F to carbon dioxide and liquid water at 60°F.

Gravity. A measure of density, usually expressed as API or specific gravity. Specific gravity is the ratio of the weight of a volume of a material to the

weight of an equal volume of distilled water. API gravity is (141.5/Sp. Gr.) − 131.5.

Grease. A solid or semisolid lubricant composed of a lubricating oil thickened with soap or other material.

GVC. Groupement Francais de Coordination, the French national member of the CEC.

HDEO. Heavy Duty Engine Oil.

Heat transfer oil. A medium used for the transfer of heat at temperatures above that of steam. High boiling petroleum oils are probably the most widely used heat transfer fluids.

Herbicidal oil. Oil used to control weeds, usually called a weed killer.

Herschel demulsibility number. A number which indicates the ability of an oil to separate from water under conditions specified in the Herschel demulsibility test.

HFU. Hy-Finishing Unit. Generally applies to a hydrotreating process where lube stocks are processed under relatively mild conditions of temperature and hydrogen pressure to improve color and stability of the oil. See Hy-Finishing.

Homogenization. The process of subjecting a lubricating grease to intimate mixing and intensive shearing action, resulting in a more uniform dispersion of components.

HTHS. High-temperature, high shear rate, usually used in connection with measuring viscosity at 150°C and 10^6 reciprocal seconds.

Humidity cabinet. A test used to evaluate the rust preventing properties of metal preservatives under conditions of high humidity, ASTM D-1748.

Hydrocarbon. Compounds containing only hydrogen and carbon. The simplest hydrocarbons are gases at ordinary temperature, but with increasing molecular weight they change to the liquid form and finally to the solid state.

Hydrocracking. A process combining cracking or pyrolysis, with hydrogenation. Feedstocks can include crudes, distillates, residua, petroleum tars, and asphalts.

Hydrofinishing. Mild hydrogenation of lube stock to replace acid and/or clay treating; see Hydrogen finishing, Hy-Finishing.

Hydrogenation. The chemical addition of hydrogen to a material. In nondestructive hydrogenation, hydrogen is added to a molecule only if, and where, unsaturation with respect to hydrogen exists. In destructive hydrogenation, the operation is carried out under conditions which result in rupture of some of the hydrocarbon chains (cracking) and hydrogen adds on when the chain breaks.

Hydrogen finishing. Mild hydrogenation of lube stock to replace acid and/or clay treating.

Hydrogen refining. Lube oil hydrorefining and hydrocracking or severe hydrotreating processes.

Hydrorefining. Severe hydrogenation of lube stock to replace furfural refining.

Hy-Finishing. Mild hydrogenation of lube stock to replace acid and/or clay treating; see Hydrofinishing, Hydrogen finishing.

IBP. Initial boiling point. The temperature at which a substance first begins to boil. In ASTM D-86 it is the temperature at which the first drop of liquid falls from the end of the condenser.

IFP. Institut Francais Du Petrole

ILMA. The Independent Lubricants Manufacturers Association.

ILSAC. The International Lubricant Standardization and Approval Committee.

IMP. Instituto Mexicano Del Petroleo.

Inhibitor. A substance, the presence of which, in small amounts in a petroleum product, prevents or retards undesirable chemical reactions from taking place in use. Their function is the prevention of oxidation and corrosion.

Ink oil. Any petroleum oil employed as vehicles for the pigments used in making printing inks.

Insulating oil. An oil used in circuit breakers, switches, transformers and other electrical apparatus for insulating and/or cooling.

IP. The Institute of Petroleum.

ISO. International Standards Organization. An organization which sets worldwide standards and classifications for lubricants.

JAMA. The Japan Automobile Manufacturers Association.

JASO. The Japan Automotive Standards Organization.

Kinematic viscosity. The ratio of the absolute viscosity of a liquid to its specific gravity at the temperature at which the viscosity is measured.

LCDU. Lube Catalytic Dewaxing Unit.

LHSV. Liquid hourly space velocity, volumes of feed per hour per unit volume of catalyst or clay.

LHV. Lower heating value of fuels; the net heat of combustion. The heat produced by complete oxidation of a fuel at 60°F to carbon dioxide and water vapor at 60°F.

LPG. Liquified petroleum gases consisting of light hydrocarbons which are gaseous at atmospheric pressure.

Lubricant. Any substance interposed between two surfaces in relation to motion for the purpose of reducing the friction and/or the wear between them.

Lubricating grease. A solid to semifluid product of dispersion of a thickening agent in a liquid lubricant. Additives imparting special properties are usually included.

Manufacturing specification. A defined range for a test which must be adhered to in the manufacture of a product.

MEK. An abbreviation for methyl ethyl ketone, a solvent used in dewaxing lube oils.

Metal deactivator. Organic compounds which suppress the catalytic action of metal compounds that normally would promote the formation of gums in products such as cracked gasoline.

Mid-continent oil. Petroleum oils derived from the central regions of the USA.

Middle distillate. Atmospheric distillation unit fractions boiling in the range of about 300 to 700°F vaporization temperature.

MIL Spec. Military specifications—a guide in determining the quality requirements of products used by the military services.

Mixed-base crude. Crude petroleum containing naphthenes (asphalt) and wax; intermediate base.

MLDW. Mobil Lube DeWaxing. A process which uses a zeolite catalyst of uniform pore size to catalytically crack wax from lube stocks rather than physically separating the wax. See LCDU.

MLSS. Mixed Liquor Suspended Solids

Molecular sieve. A synthetic zeolite mineral having pores of uniform size, capable of separating molecules based on their size and/or structure by adsorption or sieving.

MP. N-methyl-2-pyrrolidone, a ketone used as an alternate to furfural and phenol for the extraction of lubricating oil fractions.

MP refining. An extraction process used to extract aromatics from lube feedstocks to improve the viscosity index and quality of lubricating oil base stocks.

MPU. MP Unit. See MP Refining. A solvent extraction unit which uses MP to remove less desirable components from lube feedstocks.

MRV. Refers to the Mini-Rotary Viscosimeter, ASTM D- 4684.

MSDS. Material Safety Data Sheet, a document required by several government agencies which typically lists the composition of a product along with hazard information, first aid measures, toxicological information and regulatory information.

Multigrade oil. One of the multiviscosity number oils in which one combines three SAE viscosity number grades, for example SAE 10W-40.

MVMA. The Motor Vehicle Manufacturers Association of the United States.

Naphthene. A group of cyclic hydrocarbons also termed cycloparaffins. Polycyclic members are also found in the higher boiling fractions.

Naphthenic crudes. Class designation of crude oils containing predominantly naphthenes or asphaltic compounds.

Neutralization number. The quantity of acid or base which is required to neu-

tralize all acidic or basic components present in a specified quantity of a test sample.

Neutral oil. The base oils produced from the distillate or overhead fractions obtained from crude distillation.

NLGI. National Lubrication Grease Institute

NLGI number. A numerical scale for classifying the consistency range of lubricating greases, and based on the ASTM D-217 worked penetration at 25°C (77°F).

NMP. N-methyl-2-pyrrolidone; See MP.

Normal paraffin. A straight chain hydrocarbon in which no carbon atom is united with more than two other carbon atoms.

N-methyl-2-pyrrolidone. See MP.

OECD. The Organization for Economic Cooperation and Development, an organization of nations established in 1961 to promote economic growth and expansion of world trade.

OEM. Refers to an Original Equipment Manufacturer

Pale oil. A petroleum lubricating or process oil refined until its color is straw to pale yellow.

Paraffin-base crudes. Crude containing paraffin wax and practically no asphalt or naphthenes.

Paraffinic. Describing the paraffin nature or composition of crude petroleum or products therefrom.

Paraffins. A homologous series of open-chain saturated hydrocarbons of the general formula Cn H2n+2 of which methane (CH4) is the first member.

Paraffin wax. A colorless wax extracted from paraffin-base lubricating oils.

PCMO. Passenger car motor oil.

PDU. Propane Deasphalting Unit. See Deasphalting.

Penetration. An arbitrary measure of consistency (hardness) of greases, waxes and asphalt. All penetration measurements are in an inverse scale of consistency, that is, the softer the consistency, the higher the penetration number which is usually expressed as the depth in tenths of a millimeter, that the standard cone penetrates the sample under prescribed conditions of weight, time and temperature. See ASTM D-217.

Percolation. The passing of a liquid through a bed of granules or powder, e.g., the slow flow of oil through a layer of decolorizing earth.

Petrolatum. Soft petroleum material obtained from petroleum residua and consisting of amorphous wax and oil.

Pipe still. See VPS.

PNA. PolyNuclear Aromatic. A compound composed of two or more aromatic rings (see aromatic). These compounds are under close scrutiny since they are generally considered to be carcinogens.

Pour depressant. An additive which lowers the pour point of an oil containing wax by reducing the tendency of the wax to form a solid mass in the oil.

Pour point. The lowest temperature at which an oil will pour or flow when it is chilled without disturbance under definite conditions.

Pour stability. The ability of a pour depressed oil to maintain its original ASTM pour point when subjected to storage at low temperatures.

Process oil. An oil not used for lubrication but as a component of another material or carrier of other products.

Raffinate. In solvent-refining practice, that portion of the oil which remains undissolved and is not removed by the selective solvent; the solvent lean phase.

Ramsbottom carbon. An alternate test method for measuring the carbon residue of petroleum fractions. See Conradson carbon; CRS, MCRT. ASTM D-524.

Read-across. The practice of applying data developed on one oil to another, similar oil.

Reclaimed oil. A lubricating oil which after use is collected, reprocessed and reused as a lubricant or fuel.

Red oil. Originally used to describe an intermediate grade of general purpose oil. It is now used to describe any oil which is red in color.

Reprocessed oil. A lubricating oil which after use is collected, reprocessed and refortified with additives and reused.

Repulp (dewaxing). A method for removing small quantities of oil from paraffin wax by remixing in solvent and refiltering one or more times.

Re-refined oil. A lubricating oil which after use is collected, reprocessed and re-refined and sold for reuse.

Residuum. The heaviest components or bottoms remaining from distilling an oil, especially crude oil.

Resin. Polymers of unsaturated hydrocarbons from petroleum processing as in cracking or propane deasphalting. Chief uses include rubber and plastics compounding and surface coatings.

SAE. The Society of Automotive Engineers.

SAE viscosity number. An arbitrary number in a system for classifying oils, automatic transmission fluids and differential lubricants according to their viscosities. They do not connote quality.

Saponification. The interaction of fatty acids, fats or esters generally with an alkali to form the metallic salt. This salt is commonly called soap.

Saybolt color. A color standard for petroleum products. The procedure and colorimeter are described in ASTM D-156.

Saybolt furol viscosity. The time in seconds for 60 ml of fluid to flow through a standard Saybolt Furol viscosimeter. This ASTM Method D-88 is appropriate for the measurement of very viscous residua and lubricants.

Saybolt universal viscosity (SUS). The time in seconds for 60 ml of fluid to flow through a standard Saybolt Universal viscosimeter at a specified temperature. ASTM Method D-88 describes the method and apparatus.

SCF. A volume of gas as standard cubic feet measured at 14.696 psia and 60°F.

SCFB or SCF/B. Standard cubic feet per barrel; usually used to express the hydrogen treat rate or consumption in hydrogenation processes.

SDU. Solvent Dewaxing Unit. Generally a process for removing wax from a lube stock by adding a solvent (MEK and toluene), chilling and filtering. See Dewaxing.

SDW. Solvent dewaxing

Selectivity. A measure of the ability of a solvent to separate compounds of different structure, e.g. aromatics from paraffins from naphthenes.

Service factor. A quantity which relates the actual on-stream time of a process unit to the total time available for use of the unit. Frequently a ratio of the number of actual operating days divided by 365.

Shear stability. The ability of a lubricating grease to resist changes in consistency (hardness) during mechanical working.

Slack wax. The soft, oily crude wax obtained from the solvent dewaxing of paraffin distillates or lube base stocks. Slack waxes contain varying amounts of oil and must be deoiled to produce hard or finished waxes.

SNO. Solvent neutral oil

Solvent neutral oil (SNO). A paraffinic base oil which has been solvent refined, dewaxed, and finished and is ready to be used in blending or compounding.

Sour crude. A classification of crude oils containing relatively large quantities of sulfur or corrosive sulfur as compared to sweet crudes. Generally crude oils which contain greater than 0.5 to 1.0 wt % sulfur.

Space velocity. The amount of gas or liquid, usually calculated at standard conditions, that pass over or through one unit volume or weight (as of a catalyst in a continuous reactor) in unit time; LHSV or WHSV.

Stability. Resistance to chemical change.

Color. Resistance to change in color; also color hold.

Heat. Resistance to change from heat.

Sediment. Resistance to formation of sediment.

Steam. Resistance to change in presence of steam.

Storage. Resistance to change while in storage.

Thermal. Resistance to change from temperature.

STLE. The Society of Tribologists and Lubrication Engineers.

Sulfur, combined. Sulfur used in combination with other additives, fats and/or oils that is not reactive to copper at temperatures of 212°F and lower.

Sulfur, reactive. Sulfur that reacts with metals at nominal temperatures and is particularly effective in extreme pressure uses such as occur in hypoid gear lubrication.

SUS (SSU). See Saybolt universal viscosity.

Sweet crude. A classification of crude oils which are low in sulfur; usually less than 0.5 to 1.0 wt % and contain no reactive sulfur compounds.

Synthetic grease. A grease composition in which the liquid lubricant is other than mineral oil.

Synthetic oil. Any of the oils manufactured by synthesis rather than by the refining of petroleum fractions. PAO's, alkyl benzenes, dibasic acid esters, polyol esters, phosphate esters, polyglycols and silicones are examples of synthetic oils.

Texture. That property of lubricating grease which is observed when a small separate portion of it is pressed together and then slowly drawn apart.

Thickener. The solid particles which are relatively uniformly dispersed to form the structure of lubricating grease in which the liquid is held by surface tension and other physical forces.

Throughput.

Clay treating. Barrels of oil per ton of clay.

Hydrogenation. Barrels of oil per pound of catalyst.

Process units. BPCD, BPOD or metric tons per year.

Treating. The contacting of petroleum products with chemicals, clay and solvents to improve base oil quality.

Turbine oil. A well-refined oil used for lubricating steam turbines. These oils show high resistance to emulsification with water and to oxidation.

Unsulfonated residue. Portion of oil which is not acted upon when the oil is agitated with a definite amount of concentrated sulfuric acid under definite conditions.

Unworked penetration. Penetration at 25°C (77°F) of a sample of a lubricating grease which has received only minimum disturbance in transferring to a grease worker cup or dimensionally equivalent container.

Vacuum distillation. Distillation below atmospheric pressure, which lowers the distilling temperature.

Vacuum still. A still working under partial vacuum as in the distillation of heavy lubricating oils.

VDT. Vacuum Distillation Tower. Generally applies to a crude distillation tower which operates at below atmospheric pressure. See Vacuum still.

VDU. Vacuum Distillation Unit. Generally includes a VDT and associated equipment for producing distillates from the bottoms of an ADT by operating at below atmospheric pressure.

VI. Viscosity Index: a measure of the change in viscosity with temperature; ASTM D-2270.

VI improver. Generally a high molecular weight polymer additive which when added to an oil will minimize the change in viscosity of the oil with temperature, i.e., improve the viscosity index.

Viscosity. The measure of the internal friction or the resistivity to flow of a liquid. In measuring viscosities of petroleum products, the values of the viscosity are usually expressed as the number of seconds required for a certain volume of the oil to pass through a standard orifice under specified conditions.

Viscosity index (VI). An arbitrary system which has been devised for indicating the relative rate of change of viscosity of a fluid with temperature; ASTM D-2270.

VPS. Vacuum Pipe Still. See VDU. Generally includes an atmospheric as well as a vacuum tower and associated equipment for the distillation of crude into gasoline, diesel, lube distillates or cracking feedstocks and vacuum residua.

Wax. Plastic, fusible, and viscous or solid substance having a characteristic luster. Wax present in a crude oil belongs to two major varieties: paraffin wax and petrolatum.

Wax distillate. A distillate prepared by distillation of a waxy crude on a VPS. Generally requires further processing including solvent refining and dewaxing to produce a lubricant base oil.

White oil. A colorless and odorless mineral oil used in medicinal and pharmaceutical preparations and as a lubricant in food and textile industries.

WHSV. Weight hourly space velocity, weight of feed per hour per unit weight of catalyst or clay; pound per pound or kg per kg, etc.

Worked penetration. Penetration of a sample of lubricating grease which has been brought to 25°C (77°F), subjected to 60 double strokes in a standard grease worker, and penetrated without delay.

Yield. The amount of a desired product or products obtained in a given process expressed as a percentage of the feedstock. As applied to grease: the amount of grease of a given consistency which may be made with a definite amount of thickening agent.

III. UPDATING REFINERY CONSTRUCTION COSTS

Estimation of refinery costs are usually made using the Nelson–Farrar Indexes published in the *Oil & Gas Journal* on a quarterly basis. These indexes for the period 1946–1992 are reprinted as Table 1 by permission of the *Oil & Gas Journal.*

Adjusting or scaling-up refinery construction costs, I, is frequently conducted using the ratio of capacities factor, R, and unit thruput, T. An example for use of the Nelson–Farrar Indexes, N, and capacity factor is presented below.

$$I_2 = I_1(T_2/T_1)^R \qquad (1)$$

where: I_1 = The actual cost of unit T_1.

I_2 = The cost of unit 2 for the same time period as unit 1.

T_1 = The size of unit 1 for which the cost is known.

T_2 = The size of unit 2 for which a cost is being determined.

R = The capacity factor = 0.6

To estimate the current cost of unit 2 multiply the capacity of unit 1 by the ratio of the Nelson–Farrar Index, N as shown in equation (2).

$$I_2 = I_1(N_2/N_1) \tag{2}$$

where: I_1 = The old cost of unit 1.

I_2 = The cost of the new unit 2.

N_1 = Nelson–Farrar Index for the old unit 1.

N_2 = The current Nelson–Farrar Index for unit 2.

Combining equations (1) and (2) provides the following:

$$I_2 = I_1(T_2/T_1)^R(N_2/N_1) \tag{3}$$

IV. NELSON–FARRAR REFINERY CONSTRUCTION INDEXES

Year	Materials component	Labor component	Miscellaneous component	Inflation index
1946	100.0	100.0	100.0	100.0
1947	122.4	113.5	114.2	117.0
1948	139.5	128.4	122.1	132.5
1949	143.6	137.1	121.6	139.7
1950	149.5	144.0	126.4	146.2
1951	164.0	152.5	145.0	157.2
1952	164.3	163.1	153.1	163.6
1953	172.4	174.2	158.8	173.5
1954	174.6	183.3	160.7	179.8
1955	176.1	189.6	161.5	184.2
1956	190.4	198.2	180.5	195.3
1957	201.9	208.6	192.1	205.9
1958	204.1	220.4	192.4	213.9
1959	207.8	231.6	196.1	222.1
1960	207.6	241.9	200.0	226.1
1961	207.7	249.4	199.5	232.7
1962	205.9	258.9	198.8	237.6
1963	206.3	268.4	201.4	243.6

(*continued*)

Year	Materials component	Labor component	Miscellaneous component	Inflation index
1964	209.6	280.5	206.8	252.1
1965	212.0	294.4	211.6	261.4
1966	216.2	310.9	220.9	273.0
1967	219.7	331.3	226.1	286.7
1968	224.1	357.4	228.8	304.1
1969	234.9	391.8	239.3	329.0
1970	250.5	441.1	254.3	364.9
1971	265.2	499.9	268.7	406.0
1972	277.8	545.6	278.0	438.5
1973	292.3	585.2	291.4	468.0
1974	373.3	623.6	361.8	522.7
1975	421.0	678.5	415.9	575.5
1976	445.2	729.4	423.8	615.7
1977	471.3	774.1	438.2	653.0
1978	516.7	824.1	474.1	701.1
1979	573.1	879.0	515.4	756.6
1980	629.2	951.9	578.1	822.8
1981	693.2	1044.2	647.9	803.8
1982	707.6	1154.2	662.8	976.9
1983	712.4	1234.8	656.8	1025.8
1984	735.3	1278.1	665.6	1061.0
1985	739.6	1297.6	673.4	1074.4
1986	730.0	1330.0	684.4	1089.9
1987	748.9	1370.0	703.1	1121.5
1988	802.8	1045.6	732.5	1164.5
1989	829.2	1440.4	769.9	1195.9
1990	832.8	1487.7	797.5	1225.7
1991	832.3	1533.3	827.5	1252.9
1992	824.6	1579.2	837.6	1277.3
May 1993	824.6	1606.1	841.1	1298.8

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Example

Assuming a solvent refining unit of 20,000 BPOD cost $10,000,000 in 1970, find the cost for a 20,000 BPOD solvent refining unit in 1992.

From the above table find the Nelson–Farrar Index for 1980 (822.8) and the index for 1992 (1277.3). Substituting these values into Equation (3) provides the following:

$$C_Y = 20{,}000(20{,}000/10{,}000)^{0.6}(1277.3/822.8)$$
$$= 20{,}000(2)^{0.6}(1.5524)$$
$$= \$47{,}060$$

V. CONVERSION FACTORS

To convert from	To	Multiply by
angstrom	meter, m	1.0×10^{-10}
atmosphere, atm	newton/square meter, N/m^2	1.013×10^5
atmosphere	pounds per square inch, psig	4.7
atmosphere	pascal, kPa	1.1033×10^2
bar	pounds per square inch	1.4504×10
bar	newton/square meter, $N/^2$	1.0×10^5
barrel (42 gal), Bbl	cubic meter, m^3	0.159
barrel,(42 gal), Bbl	cubic feet, ft^3	5.615
barrel	U.S. gallon, gal	4.20×10
barrel per day, BPD	cubic meters/hour, m^3/hr	6.625×10^{-3}
Btu (Int'l Steam Table)	joule, J	1.055×10^3 Btu
Btu per hour	watts, W	2.929×10^{-1}
Btu per hour	horsepower, hp	2.389×10^{-1}
Btu per pound/°F	calorie/gram/°C, c/g	1.0
calorie	joule, J	4.187
centimeter of mercury	newton/square meter, N/m^2	1.333×10^3
centimeter of water	newton/square meter, N/m^2	9.806×10
centistoke	square meters/second, m^2/sec	1.0×10^{-6}
cubic centimeter, cc	cubic inch, in^3	$0.6.1 \times 10^{-2}$
cubic foot	liters, l	2.8316×10
cubic foot, ft^3	cubic meters, m^3	2.832×10^{-2}
cubic feet/barrel	m^3/m^3	0.178
cubic meter, m^3	barrel, Bbl	6.29
cubic meter, m^3	cubic feet, ft^3	3.5315×10
degree, angle	radian, rad	1.745×10^{-2}
dram, avoirdupois	kilogram, kg	1.772×10^{-3}
dram, troy	kilogram, kg	3.888×10^{-3}
dram, U.S. fluid	cubic meter, m^3	3.697×10^{-6}
dyne	newton, N	1.0×10^{-5}
electron volt	joule, J	1.60×10^{-19}
erg	joule, J	1.0×10^{-7}
fluid ounce, U.S.	cubic meter, m^3	2.96×10^{-5}
feet	meters, m	3.05×10^{-1}
gallon, imperial gal	gallon, U. S. gal	1.2009
gallon, U.S. dry	cubic meter, m^3	4.404×10^{-3}
gallon, U.S. liquid	cubic meter, m^3	3.785×10^{-3}
gallon per minute, gpm	cubic meters/minute, m^3/min	3.785×10^{-3}

gram	kilogram, kg	1.0×10^{3}
gram/cc, water	pound/cubic foot, lb/ft^2	6.24×10
horsepower	watt, W	7.457×10^{2}
horsepower, boiler	watt, W	9.81×10^{3}
horsepower, electric	watt, W	7.46×10^{2}
hundred weight, long	kilogram, kg	5.080×10
hundred weight, short	kilogram, km	4.536×10
inch	meter, m	2.54×10^{-2}
inch mercury	newton/square meter, N/m^2	3.386×10^{3}
kilogram force	newton, N	9.806
kilowatt	Btu/hour	3.412×10^{3}
kilowatt	horsepower, hp	1.3410
kilowatt	joules/hour J/hr	3.6×10^{6}
liter	cubic meter, m^3	1×10^{-3}
micron	meter, m	1.0×10^{-6}
mil	meter	2.54×10^{-6}
millibar	newton/square meter, N/m^2	1.000×10^{2}
ounce, troy	kilogram, kg	3.11×10^{-2}
ounce, U.S. liquid	kilogram, kg	2.96×10^{-5}
pascal, Pa	newton/square meter, N/m^2	1.0
poise	newton second/square meter	0.10
pound force	newton, N	4.448
pound mass	kilogram, kg	4.536×10^{-1}
pound mass, troy	kilogram, kg	3.73×10^{-1}
poundal	newton, N	1.38×10^{-1}
pounds per square inch	pascal, Pa	6.895×10^{3}
second, angle	radian, rad	4.85×10^{-6}
ton, long	kilogram, kg	1.016×10^{3}
ton, long	pound, lb	2.240×10^{3}
ton, metric	kilogram, kg	1.0×10^{3}
ton, metric	pound, lb	2.2046×10^{3}
ton, short	kilogram, kg	9.072×10^{3}
ton, short	pound, lb	2×10^{3}
torr	newton/square meter, N/m^2	1.333×10^{2}
yard	meter, m	9.14×10^{-1}

Index

Acid treating processes, 226–229
  acid alkali refining, 227
  acid-clay refining, 228
  neutralization, 228–229
  wet refining, 227
Acronyms, 262–278
Additives, 6
  for automotive lubricants, 6
  for industrial lubricants, 7
Aromatics, 20, 21
Asphaltenes, 21, 22

Baffle towers, 72, 105, 108, 109
Base oil and wax processing overview, 1–14
Base oil types and properties, 28–35
  bright stocks, 31
  comparison of dewaxing process used, 34, 195–196, 202–205, 214–218
  comparison of naphthenic and paraffinic, 30
  comparison of SNO 100 base oils, 34
  composition of 95-105 VI SNOs, 33
  conventional, 30
[Base oil types and properties]
  cylinder oils, 31
  hydrotreated naphthenes, 32
  naphthene pale oils, 31
  polyalphaolefins, 34
  solvent extracted naphthenes, 32
  solvent neutral oils, 31

Capacity of base oil plants:
  Canada, 11
  United States of America, 10–11
    leading manufacturers, 12
    trends 1976-1993, 12
  Worldwide, 8–9
Catalysts, 125, 140, 207–209, 234
Catalytic dewaxing, 194–222
  British Petroleum, 194, 196–197
  catalyst cycle time, 218–219
  catalysts, 207
  Chevron, 194, 198, 202, 203
  compared to solvent dewaxing, 195–196, 201, 202–205, 212–218
  composition of feed and products, 200, 201, 203, 209, 211–213

[Catalytic dewaxing]
effect of crude source, 218
effect of nitrogen content, 219
effect of process severity, 214
effect of reaction temperature, 221, 222
fundamentals, 204–221
Instituto Mexicano del petroleo, 204
investment costs and utility requirements, 197–198, 199–202, 204, 206
isodewaxing, 202–205
MLDW, 198–202
Mobil, 194, 198–202
process conditions, 197, 199, 202, 210–211
process variables, 204–206
Slack wax dewaxing, 202, 205
Unocal/DW, 203
Centrifugal contactors, 109, 110
Chemical treating, 3, 226–232
Clay treating processes, 229–232
contacting processes, 229
percolation processes, 230–232
Construction cost updating, 278–281
Conversion factors, 281–282
Crude oil classification, 23
Crude oil composition, 17–23
aromatics, 20, 21
asphaltenes, 21–22
isoparaffins, 19
metals, 22
nitrogen, 17, 21
olefins, 19, 20
oxygen, 17, 21
paraffins, 18
resins, 21, 22
sulfur, 17, 21
Crude oil evaluation methods, 24–28
Crude oil properties, 23–24
Cycloparaffins, 18, 19

Deasphalting, 2, 3, 53–78
devices, 72–74
design, 73
types, 72
[Deasphalting]
effect of feedstock, 53, 55
effect of pressure, 60
effect of solvent dosage, 57–59
effect of solvent-to-oil ratio, 56, 59
effect of temperature, 56, 59
effects on properties, 53, 54
feedstocks and products, 53
investment and utility requirements, 75–78
process conditions, 55
process flow, 61, 68–71
continuous units, 68–71
mixer-settler units, 61,68
process variables, 54, 55
solvent composition, 60, 62–67
solvent recovery techniques, 70–72
multiple effect evaporation, 71
supercritical, 72
yields and product properties, 56
Definitions, 262–278
Demex process, 72
Desalting, 2, 42–43
Dewaxing, 4, 153–190, 194–222
Distillation, 2, 42–51
atmospheric, 44, 46
boiling range, 46, 47 49, 50
cut points, 46
flow diagram, 44, 45
products, 44, 46
unit internals, 49
vacuum, 47, 50
Duo-Sol process, 3, 82–85

Energy reduction techniques, 113–116, 186–190
EXOL N extraction, (*see* Solvent refining)

Finishing, 4, 225–244
acid treating processes, 226–229
acid alkali refining, 227
acid-clay refining, 228
neutralization, 228–229
wet refining, 227
clay treating processes, 229–232
contacting processes, 229

[Finishing]
percolation processes, 230–232
effects on base oil, 226
hydrogen finishing, 232–243
catalysts, 234
comparison with acid-clay treating, 236
effect of catalyst, 239, 240
effect of pressure, 236
effect of temperature, 237–239
effect on base oils, 235
feedstocks, 233
process conditions, 233
process flow, 234–235
hy-starting, 238, 239
solvent refining, 244
wax finishing, 240–243
acid-clay, 240
catalysts, 240
investment costs, 241
product properties, 241–243
Formulated lubricants, 35
Formulated products, 5–6
Furfural refining, 2, 86–89

Glossary of acronyms and terms, 262–278

Hydrocracking processes, 3, 119, 121–138
base oil composition and performance, 136
blocked feed hydrocracking, 130–132
bulk feed hydrocracking, 127–130
catalysts, 124, 125
comparison with solvent extraction, 123, 124
effect of feedstock quality, 125–126
effect of temperature and space velocity, 126–127
effect on feedstock properties, 122, 123
feedstocks, 123
hydrorefining, 131–132
investment and utility requirements, 136–138
[Hydrocracking processes]
licensors, 136
process conditions, 122, 123
process flow, 121, 130, 131
process variables, 125–131
solvent extraction, 131–135
stabilization, 131
VI droop, 127–130
wax hydrocracking and isomerization, 135–136
Hydrofinishing, (*see* Hydrogen finishing)
Hydrogenation, (*see* Catalytic dewaxing, Hydrocracking, Hydrorefining, and Hydrofinishing)
Hydrogen finishing, 4, 232–243
catalysts, 234
comparison with acid-clay treating, 236
effect of catalyst, 239, 240
effect of pressure, 236
effect of temperature, 237–239
effect on base oils, 235
feedstocks, 233
process conditions, 233
process flow, 234–235
wax finishing, 240–243
Hydrogen refining processes, 3, 119–147
chemical reactions of hydrogenation processes, 119–120
hydrocracking reactions, 120–121
purification reactions, 120,121
saturation reactions, 120–121
hydrocracking processes, 121–138
hydrocracking and solvent extraction, 131–135
hydrorefining processes, 138–147
wax hydrocracking and hydroisomerization, 135
Hydrorefining processes
catalysts, 139–140
effect of feedstock quality, 141, 144
effects of temperature and space velocity, 142
feedstocks, 139
investment and utility requirements, 146

[Hydrorefining processes]
licensors, 145–146
process conditions, 139
process flow, 143, 146, 147
process variables, 140–145
Hydrotreating, (*see* Hydrogenation)
Hy-Starting, 2, 238, 239

Inert gas stripping, 89, 91, 114, 116, 187–189
Isoparaffins, 18–20

Liquid sulfur dioxide, 3, 84, 86
Lubricant base oil and wax processing overview 1–14
additives, 6, 7
base oil and wax processing, 1–14
deasphalting, 3
dewaxing, 4
distillation, 2
finishing, 4
formulated products, 5–6
manufacturing processes, 2
process flow for manufacture of naphthenic oils, 3
process flow for manufacture of paraffinic oils, 2
product formulation, 4
refining, 3
Lubricant base oil and wax profile, 6–13

Manufacturing processes, 2
effect on chemical composition and properties of base oils, 5
process flow for manufacture of naphthenic oils, 3
process flow for manufacture of paraffinic oils, 2
MP refining, (*see* Solvent refining)
Multiple effect evaporation, 71, 113, 114, 115

Naphthenes, 18–20
N-methyl-2-pyrrolidone, (*see* Solvent refining)

NMP refining, (*see* Solvent refining)
Nomenclature, 259–262
Normal paraffins, 18

Packed towers, 72
Phenol refining, (*see* Solvent refining)
Product formulation, 4

Refinery products, 24, 25
Resins, 21, 22
ROSE™, (*see* Solvent refining)
Rotating disc contactor, 72–74, 105–108

Solvent dewaxing, 153–190
chillers, 169
chilling curve, 179
dewaxing aids, 180
dewaxing differential 171–173
exchangers, 169
feedstocks, 154
filters, 180–182
cold backwashing procedure, 186
hot washing procedure, 185
operational mode, 182–183
filtration, 180–186
effect of filter speed, 184
effect of vacuum, 185
effect of wash ratio, 184
filter cloth, 183–184
filters, 180–182
filtration rate, 175
fouling of filter cloths, 185
procedure, 168, 176, 177
comparison of, 176–179
inert gas stripping, 187–189
investment costs and utility requirements, 190
ketone dewaxing processes, 155–158
A-B process, 155
Dilchill™ process, 157–158
Di/Me process, 158–159
Texaco MEK, 156–157
miscibility diagrams, 171, 172
determination of, 171–173
process steps, 156
process variables, 165

[Solvent dewaxing]
crystallization method, 167–168
dilution and chilling rate 174–179
feedstock preparation, 169–170
feedstock quality, 165
prior processing, 166
solvent and solvent composition, 170–173
determination, 171–173
effect of, 173–174
products, 154
propane dewaxing, 159–160
solvent recovery, 186–189
urea dewaxing, 160–162
Solvent extraction, (*see* Solvent refining)
Solvent extraction and hydrocracking combination, 131–134
Solvent refining, 2, 3, 81–117, 131, 132, 134, 137, 139
characteristics of ideal solvent, 82, 83
commercially used solvents, 83
comparison of major refining processes, 94
comparison of major solvents, 93
conversion of furfural and phenol units to MP, 110–113
Duo-Sol Process 82–85
flow diagram, 84
mixer, 84
settler, 85
Edeleanu liquid sulfur dioxide process, 3, 84, 86
process flow, 85
effect of crude source, 100–102
effect of impurities, 102–104
effect of recycle and temperature gradients, 104
effect of solvent and solvent dosage, 95–97
effects of temperature and dosage, 97–100
effects on feedstocks, 81, 82
energy reduction techniques, 113–116
extraction devices, 105–110
[Solvent refining]
feedstocks, 81–82
furfural refining, 86–87
process flow, 87
inert gas stripping, 114, 116
investment and utility requirements, 90, 112, 113, 116
multiple effect evaporation, 113–115
N-methyl-2-pyrrolidone refining, 88–90
flow diagrams, 88, 89
phenol refining, 90–91
process flow 91
process conditions, 95
process variables, 94–95
products, 81–82
properties of major solvents, 91–92
rates of solvent degradation, 93–95
relative use of processes, 91
structure of major solvents, 93
Speciality oils, 35, 36
Sulfur content of crude oils, 17, 22
Supply and demand of lubricant base oils, 13–14

Updating refinery construction costs, 278–281
Used oil, 247–255
as a fuel, 247, 248
comparison of reclaiming and gasification processes, 254
composition of refined oils, 252, 532
disposition of used oils, 247–248
economics, 252–254
gasification, 251, 252
properties of re-refined oils, 252
reclaiming techniques, 247, 248
recycling, 247–255
re-refining processes, 248–251
acid-clay, 249
BETC, 251
IFP type, 249–250
KTI type, 250
Mohawk, 250
PROP, 250–251
UOP DCH, 251

[Used oil]
sources of used oil, 247, 248

Waxes, 37–40
composition, 38, 211–213
properties, 38
specifications, 38, 39
types, 37
uses of, 39, 40

Wax fractionation/deoiling, 162–165
recrystallization, 163–164
spray deoiling, 164–165
sweating, 162
warm-up deoiling, 162–163
Wax hydrocracking and isomerization, 135–136
White oils, 141–147, (*see also* Speciality oils)